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| (54) Title: ETHYLENE/ALPHA-OLEFIN/DIENE INTERPOLYMERS AND THEIR PREPARATION | | |
| (57) Abstract Random ethylene/alpha-olefin/diene monomer interpolymers with an alpha-olefin distribution that is more clustered than Bernoullian are prepared using Group 4 metal constrained geometry complex catalyst and an activating cocatalyst. The catalyst includes a fused ring indenyl derivative ligand. | | |

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ETHYLENE/ALPHA-OLEFIN/DIENE INTERPOLYMERS AND THEIR PREPARATION

This invention relates to interpolymers of ethylene (C_2), at least one alpha-olefin (α -olefin), preferably propylene (C_3), butene-1, hexene-1 or octene-1, and at least one diolefin monomer, preferably a nonconjugated diene monomer, and their preparation using an olefin
5 polymerization catalyst derived from a class of Group 4 metal complexes.

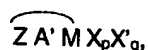
Constrained geometry metal complexes and methods for their preparation are disclosed in EP-A-416,815 (US serial number 545,403, filed July 3, 1990); EP-A-468,651 (US serial number 547,718, filed July 3, 1990); EP-A-514,828 (US serial number 702,475, filed May 20, 1991); EP-A-520,732 (US serial number 876,268, filed May 1, 1992) and WO93/19104 (US
10 serial number 8,003, filed January 21, 1993), as well as US-A-5,055,438, US-A-5,057,475, US-A-5,096,867, US-A-5,064,802, US-A-5,132,380, WO95/00526, and US Provisional Application 60-005913. Various substituted indenyl containing metal complexes are taught in US serial number 592,756, filed January 26, 1996, as well as WO95/14024. The relevant teachings of all of the foregoing patents or the corresponding US patent applications are hereby incorporated by
15 reference.

One aspect of the present invention is a random ethylene/ α -olefin/diene monomer (EAODM) interpolpolymer, the interpolpolymer having (a) a weight ratio of ethylene to α -olefin within a range of from 90:10 to 10:90, the α -olefin being a C_{3-20} α -olefin; (b) a diene monomer content within a range of from greater than 0 to 25 percent by weight (wt%), based on interpolpolymer
20 weight; and (c) a B value of from 0.94 to 1.0, the B value being determined by ^{13}C NMR (carbon-13 nuclear magnetic resonance) spectroscopy and the formula $B = P_{OE}/(2 P_E P_O)$ wherein P_E is a molar fraction of ethylene units derived from ethylene, P_O is a molar fraction of α -olefin units derived from an α -olefin, and P_{OE} is a ratio of the number of α -olefin/ethylene chains to the number of all dyad chains in the interpolpolymer. J. C. Randall, *Macromolecules*, 15, pg 353 (1982) and J. Ray, *Macromolecules*, 10, pg 773 (1977) provide further explanations of
25 the B value. A Bernoullian distribution will provide a B value of 1, a perfectly alternating polymer will provide a B value of 2 and a block polymer, such as a ethylene/propylene diblock polymer, will give a B value that approaches 0. In practical terms, a B value of less than 1 indicates that a polymer has an α -olefin distribution that is more clustered than Bernoullian and a B value of
30 more than 1 indicates that a polymer has an α -olefin distribution that is more isolated than Bernoullian.

^{13}C NMR samples for B value determination are suitably prepared in a 50%/50% (volume basis) solvent blend of 1,1,2,2-tetrachloroethane- d_2 and 1,2,4-trichlorobenzene that includes sufficient paramagnetic relaxation agent to produce an NMR solvent having a
35 concentration of 0.05 M in chromium(III) acetylacetonate. The samples are prepared by mixing

a polymer and the NMR solvent in a volumetric ratio of 10:90 in a nitrogen-purged and capped 10 millimeter (mm) NMR tube. The contents of the tube are heated to reflux periodically until homogeneity is achieved. Spectra are acquired at 130° Centigrade (°C) using an inverse gated decoupling sequence with a pulse width of 90°C and a delay of 5 - 9 seconds.

- 5 A second aspect of the present invention is a process for preparing the interpolymer of the first aspect, the process comprising contacting ethylene, at least one C₃₋₂₀ α-olefin monomer and a diene monomer with a catalyst and an activating cocatalyst, the catalyst being a metal complex that corresponds to the formula



- 10 wherein

M is titanium, zirconium or hafnium in the +2, +3 or +4 formal oxidation state;

- A' is a substituted indenyl group substituted in at least the 2 position with a group selected from hydrocarbyl, fluoro-substituted hydrocarbyl, hydrocarbyloxy-substituted hydrocarbyl, dialkylamino- substituted hydrocarbyl, silyl, germyl and mixtures thereof, said group
15 containing up to 40 nonhydrogen atoms, and said A' further being covalently bonded to M by means of a divalent Z group;

Z is a divalent moiety bound to both A' and M via σ-bonds, said Z comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

- 20 X is an anionic or dianionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π-bound ligand groups;

X' independently each occurrence is a neutral Lewis base ligating compound, having up to 20 atoms;

- p is 0, 1 or 2, and is two less than the formal oxidation state of M, with the proviso that
25 when X is a dianionic ligand group, p is 1; and

q is 0, 1 or 2.

- Preferred X' groups are carbon monoxide; phosphines, especially trimethylphosphine, triethylphosphine, triphenylphosphine and bis(1,2-dimethylphosphino)ethane; P(OR)₃, wherein R is a C₁₋₂₀ hydrocarbyl; ethers, especially tetrahydrofuran (THF); amines, especially pyridine,
30 bipyridine, tetramethylethylenediamine (TMEDA), and triethylamine; olefins; and conjugated dienes, preferably neutral conjugated dienes, having from 4 to 40 carbon atoms. Complexes including the latter X' groups include those wherein the metal is in the +2 formal oxidation state.

The above metal complexes may exist as isolated crystals, optionally in pure form or as a mixture with other complexes, in the form of a solvated adduct, optionally in a solvent, especially an organic liquid, as well as in the form of a dimer or chelated derivative thereof, wherein the chelating agent is an organic material, preferably a neutral Lewis base, especially a trihydrocarbylamine, trihydrocarbylphosphine, or halogenated derivative thereof.

Figure I is a schematic flow diagram that illustrates the process used in Examples 4-7 and Comparative Example A.

The present process results in the highly efficient production of high weight average molecular weight (M_w) EAODM interpolymers or polymers over a wide range of polymerization conditions, and especially at elevated temperatures. They are especially useful for the solution polymerization of EAODM polymers wherein the diene is 5-ethylidene-2-norbornene (ENB), 1,4-hexadiene or a similar nonconjugated diene or a conjugated diene such as 1,3-pentadiene. The use of elevated temperatures dramatically increases the productivity of such process due to the fact that increased polymer solubility at elevated temperatures allows the use of increased conversions (higher concentration of polymer product) without exceeding solution viscosity limitations of the polymerization equipment as well as reduced energy costs needed to devolatilize the reaction product.

All references to the Periodic Table of the Elements herein refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1989. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

EAODM interpolymers of the present invention have three distinct characteristics. One is a rheology ratio ($V_{0.1}/V_{100}$) at a temperature of 190°C within a range of from about 3 to about 90. A second is a Mooney Viscosity or MV (ML_{1+4} @ 125 °C, ASTM D1646-94) within a range of from 1 to 150, preferably from 10 to 120, and more preferably from 15 to 100. A third is a reactivity ratio product (RRP) within a range of from 1 to < 1.25.

When prepared at a contact temperature of from 40-185 °C, and compared to corresponding EAODM polymers prepared from the same monomers and at the same temperature using (tetramethylcyclopentadienyl)-dimethyl(t-butylamido)silanetitanium dimethyl or (tetramethylcyclopentadienyl)dimethyl (t-butylamido)-silanetitanium 1,3-pentadiene as the catalyst, EAODM polymers of the present invention offer certain improvements. For example, they have a rheology ratio that is at least 10% greater than that of the corresponding EAODM polymers. They also have a diene content that is, on a weight basis, at least 50 percent (%) greater, a M_w that is at least 1.5 times greater, a glass transition temperature (T_g), obtained from a differential scanning calorimeter (DSC) curve using the first derivative of temperature,

that is at least one °C lower and a MV that is at least 2.5 times greater than that of the corresponding EAODM polymers. For purposes of T_g comparison, the corresponding EAODM polymers have a crystallinity that is > 0 but $< 5\%$.

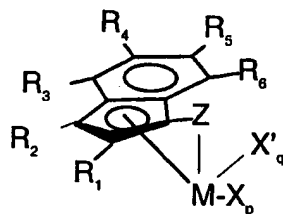
The process of the present invention may be used to polymerize C_2 together with at least one C_{3-20} α -olefin (ethylenically unsaturated) monomer and a C_{4-40} diene monomer. The α -olefin may be either an aliphatic or an aromatic compound and may contain vinylic unsaturation or a cyclic compound, such as cyclobutene, cyclopentene, and norbornene, including norbornene substituted in the 5 and 6 position with C_{1-20} hydrocarbyl groups. The α -olefin is preferably a C_{3-20} aliphatic compound, more preferably a C_{3-16} aliphatic compound. Preferred ethylenically unsaturated monomers include 4-vinylcyclohexene, vinylcyclohexane, norbornadiene and C_{3-10} aliphatic α -olefins (especially ethylene, propylene, isobutylene, butene-1, pentene-1, hexene-1, 3-methyl-1-pentene, 4-methyl-1-pentene, octene-1, decene-1 and dodecene-1), and mixtures thereof. Most preferred monomers are ethylene, and mixtures of ethylene, at least one of propylene, butene-1, hexene-1 and octene-1, and a nonconjugated diene, especially ENB.

The C_{4-40} diolefin or diene monomer is desirably a nonconjugated diolefin. The nonconjugated diolefin can be a C_{6-15} straight chain, branched chain or cyclic hydrocarbon diene. Illustrative nonconjugated dienes are straight chain acyclic dienes such as 1,4-hexadiene, 1,5-heptadiene, and 1,6-octadiene; branched chain acyclic dienes such as 5-methyl-1,4-hexadiene, 2-methyl-1,5-hexadiene, 6-methyl-1,5-heptadiene, 7-methyl-1,6-octadiene, 3,7-dimethyl-1,6-octadiene, 3,7-dimethyl-1,7-octadiene, 5,7-dimethyl-1,7-octadiene, 1,7-octadiene, 1,9-decadiene and mixed isomers of dihydromyrcene; single ring alicyclic dienes such as 1,4-cyclohexadiene, 1,5-cyclooctadiene and 1,5-cyclododecadiene; multi-ring alicyclic fused and bridged ring dienes such as tetrahydroindene, methyl tetrahydroindene, dicyclopentadiene, bicyclo-(2,2,1)-hepta-2, 5-diene (norbornadiene), methyl norbornadiene; alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes such as 5-methylene-2-norbornene (MNB), ENB, 5-vinyl-2-norbornene, 5-propenyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene and 5-cyclohexylidene-2-norbornene.

When the diolefin is a conjugated diene, it can be 1,3-pentadiene, 1,3-butadiene, 2-methyl-1,3-butadiene, 4-methyl-1,3-pentadiene, or 1,3-cyclopentadiene

The diene is preferably a nonconjugated diene selected from ENB, 1,4-hexadiene and norbornadiene, more preferably, ENB. The EAODM diene monomer content is preferably from >0 to 25 wt%, more preferably from 0.3 to 20 wt%, and most preferably from 0.5 to 15 wt%.

Preferred coordination complexes used according to the present invention are complexes corresponding to formula IA:



Formula IA

wherein:

R_1 and R_2 , independently are groups selected from hydrogen, hydrocarbyl, perfluoro substituted hydrocarbyl, silyl, germyl and mixtures thereof, said group containing up to 20 nonhydrogen atoms, with the proviso that at least one of R_1 or R_2 is not hydrogen;

R_3 , R_4 , R_5 , and R_6 independently are groups selected from hydrogen, hydrocarbyl, perfluoro substituted hydrocarbyl, silyl, germyl and mixtures thereof, said group containing up to 20 nonhydrogen atoms;

M is titanium, zirconium or hafnium;

Z is a divalent moiety comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen, said moiety having up to 60 non-hydrogen atoms;

p is 0, 1 or 2;

q is zero or one;

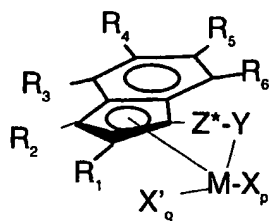
with the proviso that:

when p is 2, q is zero, M is in the +4 formal oxidation state, and X is an anionic ligand selected from the group consisting of halide, hydrocarbyl, hydrocarbyloxy, di(hydrocarbyl)amido, di(hydrocarbyl)phosphido, hydrocarbysulfido, and silyl groups, as well as halo-, di(hydrocarbyl)amino-, hydrocarbyloxy- and di(hydrocarbyl)phosphino-substituted derivatives thereof, said X group having up to 20 nonhydrogen atoms,

when p is 1, q is zero, M is in the +3 formal oxidation state, and X is a stabilizing anionic ligand group selected from the group consisting of allyl, 2-(N,N-dimethylaminomethyl)phenyl, and 2-(N,N-dimethyl)-aminobenzyl, or M is in the +4 formal oxidation state, and X is a divalent derivative of a conjugated diene, M and X together forming a metallocyclopentene group, and

when p is 0, q is 1, M is in the +2 formal oxidation state, and X' is a neutral, conjugated or nonconjugated diene, optionally substituted with one or more hydrocarbyl groups, said X' having up to 40 carbon atoms and forming a π -complex with M.

More preferred coordination complexes used according to the present invention are complexes corresponding to formula IB:



Formula IB

wherein:

5 R_1 and R_2 are hydrogen or C_{1-6} alkyl, with the proviso that at least one of R_1 or R_2 is not hydrogen;

R_3 , R_4 , R_5 , and R_6 independently are hydrogen or C_{1-6} alkyl;

M is titanium;

Y is -O-, -S-, -NR*-, -PR*-;

10 Z^* is SiR^{*}_2 , CR^{*}_2 , $SiR^{*}_2SiR^{*}_2$, $CR^{*}_2CR^{*}_2$, $CR^{*}=CR^{*}$, $CR^{*}_2SiR^{*}_2$, or GeR^{*}_2 ;

R^* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R^* having up to 20 non-hydrogen atoms, and optionally, two R^* groups from Z (when R^* is not hydrogen), or an R^* group from Z and an R^* group from Y form a ring system;

15 p is 0, 1 or 2;

q is zero or one;

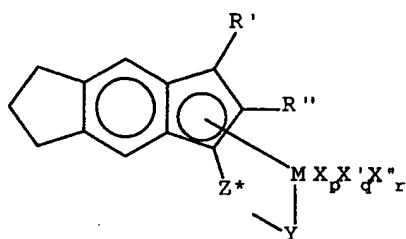
with the proviso that:

when p is 2, q is zero, M is in the +4 formal oxidation state, and X is independently each occurrence methyl or benzyl,

20 when p is 1, q is zero, M is in the +3 formal oxidation state, and X is 2-(N,N-dimethyl)aminobenzyl; or M is in the +4 formal oxidation state and X is 1,4-butadienyl, and

when p is 0, q is 1, M is in the +2 formal oxidation state, and X' is 1,4-diphenyl-1,3-butadiene, 2,4-hexadiene, or 1,3-pentadiene. The latter diene is illustrative of unsymmetrical diene groups that result in production of metal complexes that are actually mixtures of the
25 respective geometrical isomers.

Still more preferred coordination complexes used according to the present invention are complexes corresponding to formula II:



Formula II

wherein:

5 R' is hydrogen, hydrocarbyl, di(hydrocarbylamino), or a hydrocarbyleneamino group, said R' having up to 20 carbon atoms,

R'' is C₁₋₂₀ hydrocarbyl or hydrogen;

M is titanium;

Y is -O-, -S-, -NR⁺-, -PR⁺-, -NR₂⁺, or -PR₂⁺;

Z* is as previously defined;

10 R*, in each occurrence, is as previously defined;

X is a monovalent anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π -bound ligand groups;

X' is, independently in each occurrence, a neutral ligating compound having up to 20 atoms;

15 X'' is a divalent anionic ligand group having up to 60 atoms

p is 0, 1 or 2;

q is zero or 1; and

r is zero or 1;

with the proviso that:

20 when p is 2, q and r are zero, M is in the +4 formal oxidation state (or M is in the +3 formal oxidation state if Y is -NR₂⁺ or -PR₂⁺), and X is an anionic ligand selected from halide, hydrocarbyl, hydrocarbyloxy, di(hydrocarbyl)amido, di(hydrocarbyl)phosphido, hydrocarbylsulfido, and silyl groups, as well as halo-, di(hydrocarbyl)amino-, hydrocarbyloxy-, and di(hydrocarbyl)phosphino-substituted derivatives thereof, said X group having up to 30
25 nonhydrogen atoms,

when r is 1, p and q are zero, M is in the +4 formal oxidation state, and X'' is a dianionic ligand selected from the group consisting of hydrocarbadiyl, oxyhydrocarbyl, and hydrocarbylenedioxy groups, said X group having up to 30 nonhydrogen atoms,

when p is 1, q and r are zero, M is in the +3 formal oxidation state, and X is a stabilizing anionic ligand group selected from the group consisting of allyl, 2-(N,N -dimethylamino)phenyl, 2-(N,N -dimethylaminomethyl)phenyl, and 2-(N,N -dimethylamino)benzyl, and

when p and r are zero, q is 1, M is in the +2 formal oxidation state, and X' is a neutral, conjugated or nonconjugated diene, optionally substituted with one or more hydrocarbyl groups, said X' having up to 40 carbon atoms and forming a π -complex with M .

Most preferred metal complexes are those according to the previous formula (II) or (III), wherein M , X , X' , X'' , R' , R'' , Z^* , Y , p , q and r are as previously defined, with the proviso that:

when p is 2, q and r are zero, M is in the +4 formal oxidation state, and X is independently each occurrence methyl, benzyl, or halide;

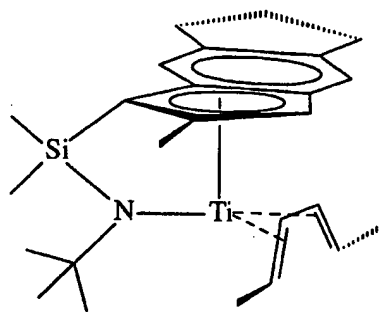
when p and q are zero, r is one, and M is in the +4 formal oxidation state, X'' is a 1,4-butadienyl group that forms a metallocyclopentene ring with M ,

when p is 1, q and r are zero, M is in the +3 formal oxidation state, and X is 2-(N,N -dimethylamino)benzyl; and

when p and r are 0, q is 1, M is in the +2 formal oxidation state, and X' is 1,4-diphenyl-1,3-butadiene or 1,3-pentadiene.

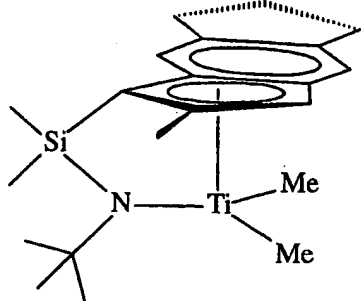
Especially preferred coordination complexes corresponding to the previous formula (II) are uniquely substituted depending on the particular end use thereof. In particular, highly useful metal complexes for use in catalyst compositions for the copolymerization of ethylene, one or more α -olefins and a diolefin comprise the foregoing complexes (II) wherein R' is as defined above, and R'' is hydrogen or methyl, especially hydrogen.

An especially preferred coordination complex, (t-butylamido)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene, is structurally represented by formula III.



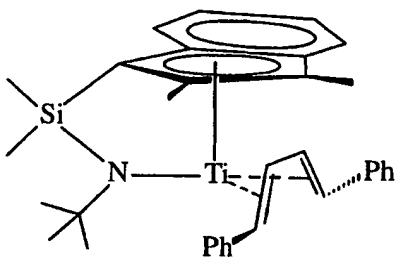
Formula III

A second especially preferred coordination complex, (t-butylamido)-dimethyl(η^5 -2-methyl-s-indacen-1-yl)silane-titanium (IV) dimethyl, is structurally represented by formula IV.



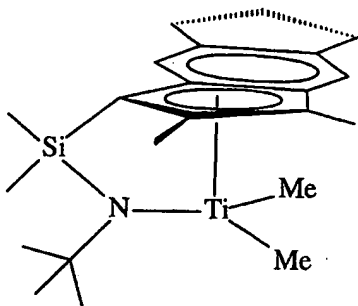
Formula IV

- 5 A third especially preferred coordination complex, (t-butylamido)-dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, is structurally represented by formula V.



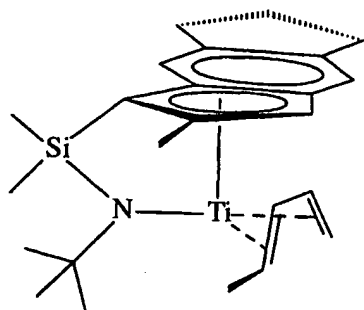
Formula V

- 10 A fourth especially preferred coordination complex, (t-butyl-amido)-dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, is structurally represented by formula VI.

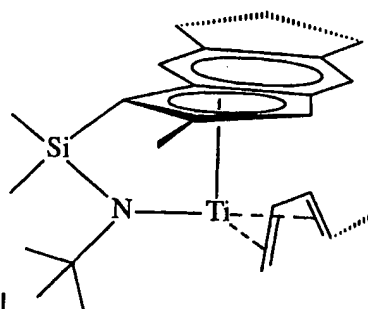


Formula VI

- 15 A fifth especially preferred coordination complex, (t-butylamido)-dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, has two isomers, sometimes referred to as geometric isomers, represented by Formulae VII and VIII.



Formula VII



Formula VIII

One group of preferred metal complexes includes: (t-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butyl-amido)-dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)-dimethyl(η^5 -2-methylindenyl)-silanetitanium (II) 2,4-hexadiene, (t-butylamido)-dimethyl(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)-dimethyl(η^5 -2-methylindenyl)silanetitanium (IV) dimethyl, (t-butylamido)dimethyl(η^5 -2-methyl-indenyl)silane-titanium (IV) dibenzyl, (t-butyl-amido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butyl-amido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)-dimethoxy(η^5 -2-methylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)dimethoxy(η^5 -2-methylindenyl)-silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)dimethoxy(η^5 -2-methylindenyl)-silanetitanium (IV) dimethyl, (t-butylamido)-dimethoxy(η^5 -2-methylindenyl)silane-titanium (IV) dibenzyl, (t-butylamido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butyl-amido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)-diisopropoxy(η^5 -2-methyl-indenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)diisopropoxy(η^5 -2-methylindenyl)silane-titanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)diisopropoxy(η^5 -2-methylindenyl)-silanetitanium (IV) dimethyl, (t-butylamido)-diisopropoxy(η^5 -2-methylindenyl)-silanetitanium (IV) dibenzyl, (t-butylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)-ethoxymethyl(η^5 -2-methylindenyl)silane-titanium (III) 2-(N,N-dimethylamino)benzyl, (t-butyl-amido)ethoxymethyl(η^5 -2-methylindenyl)-silanetitanium (IV) dimethyl, (t-butylamido)ethoxy-methyl(η^5 -2-methylindenyl)silanetitanium (IV) dibenzyl, (t-butylamido)dimethyl(η^5 -2-ethyl-indenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethyl(η^5 -2-ethylindenyl)-silane-titanium (II) 1,3-pentadiene, (t-butylamido)-dimethyl(η^5 -2-ethylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)dimethyl(η^5 -2-ethylindenyl)silanetitanium (III) 2-(N,N-dimethyl-amino)benzyl, (t-butylamido)dimethyl(η^5 -2-ethylindenyl)silanetitanium (IV) dimethyl, (t-butyl-amido)dimethyl(η^5 -2-ethylindenyl)silanetitanium (IV)

- dibenzyl, (t-butylamido)dimethoxy(η^5 -2-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethoxy(η^5 -2-ethylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)dimethoxy(η^5 -2-ethylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)dimethoxy(η^5 -2-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)-dimethoxy(η^5 -2-ethylindenyl)silanetitanium (IV) dimethyl, (t-butylamido)dimethoxy(η^5 -2-ethylindenyl)silanetitanium (IV) dibenzyl, (t-butylamido)-diisopropoxy(η^5 -2-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)-diisopropoxy(η^5 -2-ethylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)diisopropoxy(η^5 -2-ethylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)diisopropoxy(η^5 -2-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)diisopropoxy(η^5 -2-ethylindenyl)silanetitanium (IV) dimethyl, (t-butylamido)-diisopropoxy(η^5 -2-ethylindenyl)silanetitanium (IV) dibenzyl, (t-butylamido)ethoxymethyl(η^5 -2-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)ethoxymethyl(η^5 -2-ethylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)ethoxymethyl(η^5 -2-ethylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)-ethoxymethyl(η^5 -2-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)-ethoxymethyl(η^5 -2-ethylindenyl)silanetitanium (IV) dimethyl, (t-butylamido)ethoxymethyl(η^5 -2-ethylindenyl)silanetitanium (IV) dibenzyl, (t-butylamido)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)-dimethyl(η^5 -2-methyl-s-indacen-1-yl)silane-titanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, (t-butylamido)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (t-butylamido)dimethoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)-dimethoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)dimethoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)dimethoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, (t-butylamido)dimethoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (t-butylamido)diisopropoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)diisopropoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)diisopropoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)diisopropoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)diisopropoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, (t-butylamido)diisopropoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (t-butylamido)ethoxymethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)ethoxymethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)ethoxymethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)-ethoxymethyl(η^5 -2-methyl-s-

- indacen-1-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butyl-amido)ethoxymethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, (t-butylamido)ethoxy-methyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (t-butylamido)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)-silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)-silanetitanium (II) 1,3-pentadiene, (t-butylamido)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silane-titanium (II) 2,4-hexadiene, (t-butylamido)-dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butyl-amido)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, (t-butylamido)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (t-butyl-amido)dimethoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butyl-amido)dimethoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butyl-amido)dimethoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)-dimethoxy(η^5 -2-ethyl-s-indacen-1-yl)silane-titanium (III) 2-(N,N-dimethylamino)benzyl, (t-butyl-amido)dimethoxy(η^5 -2-ethyl-s-indacen-1-yl)-silanetitanium (IV) dimethyl, (t-butylamido)-dimethoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (t-butylamido)diisopropoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)diisopropoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)diisopropoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)diisopropoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (III) 2-(N,N-dimethylamino)-benzyl, (t-butylamido)diisopropoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, (t-butyl-amido)diisopropoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (t-butylamido)ethoxy-methyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)ethoxy-methyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)ethoxymethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)ethoxymethyl(η^5 -2-ethyl-s-indacen-1-yl)-silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)ethoxymethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, (t-butylamido)ethoxymethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (dimethylamine)dimethyl(η^5 -2-methylindenyl)silanetitanium (III) dimethyl, (dimethylamine)-dimethyl(η^5 -2-methylindenyl)silanetitanium (III) dibenzyl, (diisopropylamine)dimethyl(η^5 -2-methylindenyl)silanetitanium (III) dimethyl, (diisopropylamine)dimethyl(η^5 -2-methylindenyl)-silanetitanium (III) dibenzyl, (di-n-butylamine)dimethyl(η^5 -2-methylindenyl)-silanetitanium (III) dimethyl, (di-n-butylamine)dimethyl(η^5 -2-methylindenyl)silanetitanium (III) dimethyl, (di-n-butylamine)dimethyl(η^5 -2-methylindenyl)silanetitanium (III) dimethyl, (di-iso-butylamine)dimethyl(η^5 -2-methylindenyl)silanetitanium (III) dimethyl, (di-iso-butylamine)dimethyl(η^5 -2-methylindenyl)silanetitanium (III) dibenzyl, (dimethylamine)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (III) dimethyl, (dimethylamine)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (III) dibenzyl, (diisopropylamine)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silane-titanium (III) dimethyl, (diisopropylamine)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silane-titanium (III) dibenzyl, (di-n-butylamine)-dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (III) dimethyl, (di-n-butylamine)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (III) dibenzyl, (di-

isobutyl-amine)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silane-titanium (III) dimethyl, (di-isobutyl-amine)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silane-titanium (III) dibenzyl, (dimethylamine)-dimethyl(η^5 -2-ethylindenyl)silane-titanium (III) dimethyl, (dimethylamine)dimethyl(η^5 -2-ethylindenyl)silane-titanium (III) dibenzyl, (diisopropylamine)dimethyl-(η^5 -2-ethylindenyl)silane-titanium (III) dimethyl, (diisopropylamine)dimethyl(η^5 -2-ethylindenyl)silane-titanium (III) dibenzyl, (di-n-butylamine)-dimethyl(η^5 -2-ethylindenyl)silane-titanium (III) dimethyl, (di-n-butylamine)dimethyl-(η^5 -2-ethyl-indenyl)silane-titanium (III) dibenzyl, (di-iso-butylamine)dimethyl(η^5 -2-ethylindenyl)-silane-titanium (III) dimethyl, (di-iso-butylamine)dimethyl(η^5 -2-ethylindenyl)silane-titanium (III) dibenzyl, (dimethylamine)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silane-titanium (III) dimethyl, (dimethylamine)-dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silane-titanium (III) dibenzyl, (diisopropylamine)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silane-titanium (III) dimethyl, (diisopropylamine)-dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silane-titanium (III) dibenzyl, (di-n-butylamine)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silane-titanium (III) dimethyl, (di-n-butylamine)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silane-titanium (III) dibenzyl, (di-iso-butylamine)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silane-titanium (III) dimethyl, (di-iso-butylamine)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silane-titanium (III) dibenzyl, Preferred members of this group include: (t-butylamido)-dimethyl(η^5 -2-methyl-s-indacen-1-yl)silane-titanium (IV) dimethyl and (t-butylamido)dimethyl(η^5 -2-methylindenyl)-silane-titanium (II) 2,4-hexadiene.

A second group of preferred catalysts includes: (t-butylamido)-dimethyl(η^5 -2,3-dimethylindenyl)silane-titanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)-dimethyl(η^5 -2,3-dimethylindenyl)silane-titanium (II) 1,3-pentadiene, (t-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silane-titanium (II) 2,4-hexadiene, (t-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silane-titanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)-silane-titanium (IV) dimethyl, (t-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silane-titanium (IV) dibenzyl, (t-butylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silane-titanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silane-titanium (II) 1,3-pentadiene, (t-butylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silane-titanium (II) 2,4-hexadiene, (t-butylamido)-dimethoxy(η^5 -2,3-dimethylindenyl)silane-titanium (III) 2-(N,N-imethylamino)benzyl, (t-butylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silane-titanium (IV) dimethyl, (t-butylamido)dimethoxy-(η^5 -2,3-dimethylindenyl)silane-titanium (IV) dibenzyl, (t-butylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)silane-titanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)diisopropoxy-(η^5 -2,3-dimethylindenyl)silane-titanium (II) 1,3-pentadiene, (t-butylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)silane-titanium (II) 2,4-hexadiene, (t-butylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)silane-titanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)silane-titanium (IV) dimethyl, (t-butylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)-silane-titanium (IV) dibenzyl, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silane-titanium

- (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silane-titanium (II) 1,3-pentadiene, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silane-titanium (II) 2,4-hexadiene, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silane-titanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silane-titanium (IV)
- 5 dimethyl, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silane-titanium (IV) dibenzyl, (t-butylamido)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (II) 1,3-pentadiene, (t-butylamido)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (II) 2,4-hexadiene, (t-butylamido)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (III) 2-(N,N-
- 10 dimethylamino)benzyl, (t-butylamido)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (IV) dimethyl, (t-butylamido)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (IV) dibenzyl, (t-butylamido)dimethoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (II) 1,3-pentadiene, (t-butylamido)dimethoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (II) 2,4-
- 15 hexadiene, (t-butylamido)dimethoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)dimethoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (IV) dimethyl, (t-butylamido)dimethoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (IV) dibenzyl, (t-butylamido)diisopropoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (II) 1,4-
- 20 diphenyl-1,3-butadiene, (t-butylamido)diisopropoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (II) 1,3-pentadiene, (t-butylamido)diisopropoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (II) 2,4-hexadiene, (t-butylamido)diisopropoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)diisopropoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-
- 25 titanium (IV) dimethyl, (t-butylamido)diisopropoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (IV) dibenzyl, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (II) 1,3-pentadiene, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (II) 2,4-hexadiene, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethyl-s-
- 30 indacen-1-yl)silane-titanium (IV) dimethyl, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (IV) dibenzyl, (dimethylamine)dimethyl(η^5 -2,3-dimethyl-indenyl)silane-titanium (III) dimethyl, (dimethylamine)dimethyl(η^5 -2,3-dimethylindenyl)silane-titanium (III) dibenzyl, (diisopropylamine)dimethyl(η^5 -2,3-dimethylindenyl)silane-titanium (III) dimethyl, (diisopropylamine)dimethyl(η^5 -2,3-dimethylindenyl)silane-titanium (III) dibenzyl, (di-n-butylamine)dimethyl(η^5 -2,3-dimethylindenyl)silane-titanium (III) dimethyl, (di-n-butylamine)-dimethyl(η^5 -2,3-dimethyl-
- 35 indenyl)silane-titanium (III) dibenzyl, (di-iso-butylamine)dimethyl(η^5 -2,3-dimethylindenyl)silane-titanium (III) dimethyl, (di-iso-butylamine)dimethyl(η^5 -2,3-dimethylindenyl)-silane-titanium (III) dimethyl, (di-iso-butylamine)dimethyl(η^5 -2,3-dimethylindenyl)-silane-titanium (III) dimethyl, (dimethylamine)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (III) dimethyl,

- (dimethylamine)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) dibenzyl,
 (diisopropylamine)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) dimethyl,
 (diisopropylamine)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) dibenzyl, (di-n-butylamine)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) dimethyl, (di-n-butyl-
 5 amine)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) dibenzyl, (di-isobutylamine)-
 dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) dimethyl, (di-isobutylamine)dimethyl-
 (η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) dibenzyl, (t-butylamido)dimethyl(η^5 -2-methyl-
 3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethyl(η^5 -2-methyl-
 3-ethylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethyl-
 10 indenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethyl-indenyl)-
 silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethyl-
 indenyl)silanetitanium (IV) dimethyl, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silane-
 titanium (IV) dibenzyl, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-
 diphenyl-1,3-butadiene, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silane-titanium (II)
 15 1,3-pentadiene, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 2,4-
 hexadiene, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-
 dimethylamino)benzyl, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV)
 dimethyl, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
 (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-
 20 butadiene, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-
 pentadiene, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 2,4-
 hexadiene, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-
 dimethylamino)benzyl, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV)
 dimethyl, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
 25 (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-
 butadiene, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-
 pentadiene, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 2,4-
 hexadiene, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-
 dimethylamino)benzyl, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV)
 30 dimethyl, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
 (t-butylamido)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-
 butadiene, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (II) 1,3-
 pentadiene, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (II) 2,4-
 hexadiene, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (III) 2-(N,N-
 35 dimethylamino)benzyl, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium
 (IV) dimethyl, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (IV)
 dibenzyl, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (II) 1,4-

diphenyl-1,3-butadiene, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (II) 1,3-pentadiene, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (II) 2,4-hexadiene, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (IV) dimethyl, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (IV) dibenzyl, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (II) 1,3-pentadiene, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (II) 2,4-hexadiene (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)-diisopropoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (IV) dimethyl, (t-butylamido)-diisopropoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (IV) dibenzyl, (t-butylamido)-ethoxymethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (II) 1,3-pentadiene, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (II) 2,4-hexadiene, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (IV) dimethyl, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (IV) dibenzyl, (dimethylamine)dimethyl(η^5 -2-methyl-3-ethylindenyl)silane-titanium (III) dimethyl, (dimethylamine)dimethyl(η^5 -2-methyl-3-ethylindenyl)silane-titanium (III) dibenzyl, (diisopropylamine)dimethyl(η^5 -2-methyl-3-ethylindenyl)silane-titanium (III) dimethyl, (diisopropylamine)dimethyl(η^5 -2-methyl-3-ethylindenyl)silane-titanium (III) dibenzyl, (di-n-butylamine)dimethyl(η^5 -2-methyl-3-ethylindenyl)silane-titanium (III) dimethyl, (di-n-butylamine)-dimethyl(η^5 -2-methyl-3-ethylindenyl)silane-titanium (III) dibenzyl, (di-iso-butylamine)dimethyl(η^5 -2-methyl-3-ethylindenyl)silane-titanium (III) dimethyl, (di-iso-butylamine)dimethyl(η^5 -2-methyl-3-ethylindenyl)silane-titanium (III) dibenzyl, (dimethylamine)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (III) dimethyl, (dimethylamine)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (III) dibenzyl, (diisopropylamine)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (III) dimethyl, (diisopropylamine)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (III) dibenzyl, (di-n-butylamine)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (III) dimethyl, (di-n-butylamine)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (III) dibenzyl, (di-iso-butylamine)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (III) dimethyl, (di-iso-butylamine)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (III) dibenzyl. Preferred members of this group include: (t-butylamido)-dimethyl(η^5 -2,3-dimethylindenyl)silane-titanium (II) 1,4-diphenyl-1,3-butadiene and (t-butylamido)-dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (IV) dimethyl.

The complexes can be prepared by use of well known synthetic techniques. Optionally a reducing agent can be employed to produce the lower oxidation state complexes. Such a process is disclosed in USSN 8/241,523, filed May 13, 1994, published as WO95-00526, the teachings of which are incorporated herein by reference. The syntheses are conducted in a suitable noninterfering solvent at a temperature from -100 to 300 °C, preferably from -78 to 100 °C, most preferably from 0 to 50 °C. "Reducing agent", as used herein, means a metal or compound that, under reducing conditions, causes a metal M to be reduced from a higher to a lower oxidation state. Examples of suitable metal reducing agents are alkali metals, alkaline earth metals, aluminum and zinc, alloys of alkali metals or alkaline earth metals such as sodium/mercury amalgam and sodium/potassium alloy. Examples of suitable reducing agent compounds are sodium naphthalenide, potassium graphite, lithium alkyls, lithium or potassium alkadienyls; and Grignard reagents. Preferred reducing agents include the alkali metals or alkaline earth metals, especially lithium and magnesium metal.

Suitable reaction media for formation of the catalyst complexes include aliphatic and aromatic hydrocarbons, ethers, and cyclic ethers, particularly branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; aromatic and hydrocarbyl-substituted aromatic compounds such as benzene, toluene, and xylene, C₁₋₄ dialkyl ethers, C₁₋₄ dialkyl ether derivatives of (poly)alkylene glycols, and tetrahydrofuran (THF). Mixtures of the foregoing are also suitable.

The complexes are rendered catalytically active by combining them with an activating cocatalyst or by use of an activating technique. Suitable activating cocatalysts for use herein include polymeric or oligomeric alumoxanes, especially methylalumoxane, triisobutyl aluminum modified methylalumoxane, or isobutylalumoxane; neutral Lewis acids, such as C₁₋₃₀ hydrocarbyl substituted Group 13 compounds, especially tri(hydrocarbyl)aluminum- or tri(hydrocarbyl)boron compounds and halogenated (including perhalogenated) derivatives thereof, having from 1 to 10 carbon atoms in each hydrocarbyl or halogenated hydrocarbyl group, more especially perfluorinated tri(aryl)boron compounds, and most especially tris(pentafluorophenyl)borane (hereinafter "FAB"); nonpolymeric, compatible, noncoordinating, ion forming compounds (including the use of such compounds under oxidizing conditions), especially the use of ammonium-, phosphonium-, oxonium-, carbonium-, silylium- or sulfonium-salts of compatible, noncoordinating anions, or ferrocenium salts of compatible, noncoordinating anions; and combinations of the foregoing activating cocatalysts and techniques. The foregoing activating cocatalysts and activating techniques have been previously taught with respect to different metal complexes in the following references: EP-A-277,003, US-A-5,153,157, US-A-

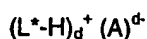
5,064,802, EP-A-468,651 (equivalent to U. S. Serial No. 07/547,718), EP-A-520,732 (equivalent to U. S. Serial No. 07/876,268), and EP-A-520,732 (equivalent to U. S. Serial Nos. 07/884,966 filed May 1, 1992), the teachings of which are incorporated herein by reference.

Combinations of neutral Lewis acids, especially the combination of a trialkyl aluminum compound having from 1 to 4 carbon atoms in each alkyl group and a halogenated tri(hydrocarbyl)boron compound having from 1 to 20 carbon atoms in each hydrocarbyl group, especially FAB, further combinations of such neutral Lewis acid mixtures with a polymeric or oligomeric alumoxane, and combinations of a single neutral Lewis acid, especially FAB with a polymeric or oligomeric alumoxane are especially desirable activating cocatalysts. Preferred molar ratios of Group 4 metal complex:FAB:alumoxane are from 1:1:1 to 1:5:20, more preferably from 1:1:1.5 to 1:5:10. The use of lower levels of alumoxane in the process of the present invention allows for production of EAODM polymers with high catalytic efficiencies using less of the expensive alumoxane cocatalyst. Additionally, polymers with lower levels of aluminum residue, and hence greater clarity, are obtained.

Suitable ion forming compounds that are useful as cocatalysts comprise a cation which is a Brönsted acid capable of donating a proton, and a compatible, noncoordinating anion, A⁻. As used herein, the term "noncoordinating" means an anion or substance that either does not coordinate to the Group 4 metal containing precursor complex and the catalytic derivative derived therefrom, or is only weakly coordinated to such complexes, thereby remaining sufficiently labile to be displaced by a neutral Lewis base. A noncoordinating anion specifically refers to an anion that, when functioning as a charge balancing anion in a cationic metal complex, does not transfer an anionic substituent or fragment thereof to the cation thereby forming neutral complexes. "Compatible anions" are anions that are not degraded to neutrality when the initially formed complex decomposes and are noninterfering with desired subsequent polymerization or other uses of the complex.

Preferred anions contain a single coordination complex comprising a charge-bearing metal or metalloid core and are capable of balancing the charge of the active catalyst species (the metal cation) that may be formed when the two components are combined. Also, said anion should be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated compounds or other neutral Lewis bases such as ethers or nitriles. Suitable metals include, but are not limited to, aluminum, gold and platinum. Suitable metalloids include, but are not limited to, boron, phosphorus, and silicon. Compounds containing anions that comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially.

Preferably such cocatalysts may be represented by the following general formula:



wherein:

L^* is a neutral Lewis base;

5 $(L^*-H)^+$ is a Brönsted acid;

A^{d-} is a noncoordinating, compatible anion having a charge of d^- , and

d is an integer from 1 to 3.

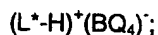
More preferably A^{d-} corresponds to the formula: $[M'Q_d]^-$;

wherein:

10 M' is boron or aluminum in the +3 formal oxidation state; and

Q is, independently for each occurrence, selected from hydride, dialkylamido, halide, hydrocarbyl, hydrocarbyloxy, halosubstituted-hydrocarbyl, halosubstituted hydrocarbyloxy, and halo-substituted silylhydrocarbyl radicals (including perhalogenated hydrocarbyl-perhalogenated hydrocarbyloxy- and perhalogenated silylhydrocarbyl radicals), said Q having up to 20 carbons with the proviso that in not more than one occurrence is Q a halide. Examples of suitable hydrocarbyloxy Q groups are disclosed in US-A- 5,296,433, the teachings of which are incorporated herein by reference.

In a more preferred embodiment, d is one, that is, the counter ion has a single negative charge and is A^- . Activating cocatalysts comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:



wherein:

L^* is as previously defined;

B is boron in a formal oxidation state of 3; and

25 Q is a hydrocarbyl-, hydrocarbyloxy-, fluorinated hydrocarbyl-, fluorinated hydrocarbyloxy-, or fluorinated silylhydrocarbyl- group of up to 20 nonhydrogen atoms, with the proviso that in not more than one occasion is Q hydrocarbyl.

Most preferably, Q is each occurrence a fluorinated aryl group, especially, a pentafluorophenyl group.

30 Illustrative, but not limiting, examples of boron compounds that may be used as an activating cocatalyst in the preparation of the improved catalysts of this invention are: tri-

substituted ammonium salts such as trimethylammonium tetrakis(pentafluorophenyl) borate, di(hydrogenated-tallowalkyl)methylammonium tetrakis(pentafluorophenyl) borate, triethylammonium tetrakis(pentafluorophenyl) borate, tripropylammonium tetrakis(pentafluorophenyl) borate, tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate, tri(sec-butyl)-

5 ammonium tetrakis(pentafluorophenyl) borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate, N,N-dimethylanilinium n-butyltris(pentafluorophenyl) borate, N,N-dimethylanilinium benzyltris(pentafluorophenyl) borate, N,N-dimethylanilinium tetrakis(4-(t-butyl-dimethylsilyl)-2, 3, 5, 6-tetrafluorophenyl) borate, N,N-dimethylanilinium tetrakis(4-(triisopropylsilyl)-2, 3, 5, 6-tetrafluorophenyl) borate, N,N-dimethylanilinium pentafluorophenoxytris(pentafluorophenyl)

10 borate, N,N-diethylanilinium tetrakis(pentafluorophenyl) borate, N,N-dimethyl-2,4,6-trimethylanilinium tetrakis(pentafluorophenyl) borate, trimethylammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate, triethylammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate, tripropylammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate, N,N-dimethylanilinium tetrakis(2,3,4,6-tetrafluorophenyl) borate, N,N-diethylanilinium tetrakis(2,3,4,6-tetrafluorophenyl) borate, and

15 N,N-dimethyl-2,4,6-trimethylanilinium tetrakis(2,3,4,6-tetrafluorophenyl) borate; dialkyl ammonium salts such as: di-(i-propyl)ammonium tetrakis(pentafluorophenyl) borate, a tri(n-butyl)ammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate, dimethyl(t-butyl)ammonium tetrakis(2,3,4,6-tetrafluorophenyl) and dicyclohexylammonium tetrakis(pentafluorophenyl) borate; tri-substituted phosphonium salts such as: triphenylphosphonium tetrakis(pentafluorophenyl)

20 borate, tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl) borate, and tri(2,6-dimethylphenyl)-phosphonium tetrakis(pentafluorophenyl) borate; di-substituted oxonium salts such as: diphenyloxonium tetrakis(pentafluorophenyl) borate, di(o-tolyl)oxonium tetrakis(pentafluorophenyl) borate, and di(2,6-dimethylphenyl)oxonium tetrakis(pentafluorophenyl) borate; di-substituted sulfonium salts such as: diphenylsulfonium tetrakis(pentafluorophenyl) borate, di(o-tolyl)sulfonium tetrakis(pentafluorophenyl) borate, and bis(2,6-dimethylphenyl)sulfonium

25 tetrakis(pentafluorophenyl) borate.

Preferred (L⁺-H)⁺ cations are N,N-dimethylanilinium and tributylammonium.

Another suitable ion forming, activating cocatalyst comprises a compound that is a salt of a carbenium ion and a noncoordinating, compatible anion represented by the formula:

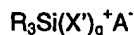
30 $\text{C}^+ \text{A}^-$

wherein:

C^+ is a C₁₋₂₀ carbenium ion; and

A^- is as previously defined. A preferred carbenium ion is the trityl cation, that is triphenylmethyl cation.

A further suitable ion forming, activating cocatalyst comprises a compound which is a salt of a silylium ion and a noncoordinating, compatible anion represented by the formula:



wherein:

5 R is C₁₋₁₀ hydrocarbyl, and X', q and A⁻ are as previously defined.

Preferred silylium salt activating cocatalysts are trimethylsilylium tetrakis(pentafluorophenyl)borate, triethylsilylium tetrakis(pentafluorophenyl)borate and ether substituted adducts thereof. Silylium salts have been previously generically disclosed in J. Chem Soc. Chem. Comm., 1993, 383-384, as well as Lambert, J. B., et al., Organometallics, 10 1994, 13, 2430-2443. The use of the above silylium salts as activating cocatalysts for addition polymerization catalysts is claimed in US serial number 304,314, filed September 12, 1994, published in equivalent form as WO96/08519 on March 21, 1996, the teachings of which are incorporated herein by reference.

Certain complexes of alcohols, mercaptans, silanols, and oximes with FAB are also 15 effective catalyst activators and may be used according to the present invention. Such cocatalysts are disclosed in US-A-5,296,433, the teachings of which are incorporated herein by reference.

The foregoing activating cocatalysts may also be used in combination. An especially preferred combination is a mixture of a tri(hydrocarbyl)aluminum or tri(hydrocarbyl)borane 20 compound having from 1 to 4 carbons in each hydrocarbyl group with an oligomeric or polymeric alumoxane compound.

The molar ratio of catalyst/cocatalyst employed preferably ranges from 1:10,000 to 100:1, more preferably from 1:5000 to 10:1, most preferably from 1:1000 to 1:1. Alumoxane, when used by itself as an activating cocatalyst, is employed in large quantity, generally at least 25 100 times the quantity of metal complex on a molar basis (calculated on moles of aluminum (Al)). FAB, when used as an activating cocatalyst, is employed in a molar ratio to the metal complex of from 0.5:1 to 10:1, more preferably from 1:1 to 6:1 most preferably from 1:1 to 5:1. The remaining activating cocatalysts are generally employed in approximately equimolar quantity with the metal complex.

30 In general, polymerization may be accomplished at conditions well known in the art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from 0-250 °C, preferably 30 to 200 °C and pressures from atmospheric to 10,000 atmospheres. Suspension, solution, slurry, gas phase, solid state powder polymerization or other process condition may be employed if desired. A support, especially silica, alumina, or a polymer

(especially poly(tetrafluoroethylene) or a polyolefin) may be employed, and desirably is employed when the catalysts are used in a gas phase polymerization process. The support is preferably employed in an amount to provide a weight ratio of catalyst (based on metal):support from 1:100,000 to 1:10, more preferably from 1:50,000 to 1:20, and most preferably from 1:10,000 to 1:30. In most polymerization reactions, the molar ratio of catalyst:polymerizable compounds employed is from 10^{-12} :1 to 10^{-1} :1, more preferably from 10^{-9} :1 to 10^{-5} :1.

Inert liquids are suitable solvents for polymerization. Examples include straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; perfluorinated hydrocarbons such as perfluorinated C_{4-10} alkanes; and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene, and ethylbenzene. Suitable solvents also include liquid olefins that may act as monomers or comonomers including butadiene, cyclopentene, 1-hexene, 1-hexane, 4-vinylcyclohexene, vinylcyclohexane, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decene, styrene, divinylbenzene, allylbenzene, and vinyltoluene (including all isomers alone or in admixture). Mixtures of the foregoing are also suitable. If desired, normally gaseous olefins can be converted to liquids by application of pressure and used herein.

The catalysts may be utilized in combination with at least one additional homogeneous or heterogeneous polymerization catalyst in separate reactors connected in series or in parallel to prepare polymer blends having desirable properties. An example of such a process is disclosed in WO 94/00500, equivalent to U. S. Serial Number 07/904,770, as well as U. S. Serial Number 08/10958, filed January 29, 1993, the teachings of which are incorporated herein by reference.

By using these catalysts in the process of the present invention, interpolymers having high comonomer incorporation and correspondingly low density, yet having a high MV are readily prepared. That is, high M_w polymers are readily attained by use of the present catalysts even at elevated reactor temperatures. This result is highly desirable because the M_w of α -olefin interpolymers can be readily reduced by the use of hydrogen or similar chain transfer agent, however increasing the molecular weight of α -olefin interpolymers is usually only attainable by reducing the polymerization temperature of the reactor. Disadvantageously, operation of a polymerization reactor at reduced temperatures significantly increases the cost of operation since heat must be removed from the reactor to maintain the reduced reaction temperature, while at the same time heat must be added to the reactor effluent to vaporize the solvent. In addition, productivity is increased due to improved polymer solubility, decreased solution viscosity, and a higher polymer concentration. Utilizing the present catalysts, α -olefin

homopolymers and copolymers having densities from 0.85 g/cm³ to 0.96 g/cm³, and a MV of from 1 to 150 are readily attained in a high temperature process.

The catalysts used in the process of the present invention are particularly advantageous for the production of interpolymers that have high levels of long chain branching. The use of the catalysts in continuous polymerization processes, especially continuous solution polymerization processes, allows for elevated reactor temperatures that favor the formation of vinyl terminated polymer chains that may be incorporated into a growing polymer, thereby giving a long chain branch. The unique combination of elevated reactor temperatures, high molecular weight (or low melt indices) at high reactor temperatures and high comonomer reactivity advantageously allows for the economical production of polymers having excellent physical properties and processability.

The process used to prepare the EAODM interpolymers of the present invention may be either a solution or slurry process both of which are previously known in the art. Kaminsky, J. Poly. Sci., Vol. 23, pp. 2151-64 (1985) reported the use of a soluble bis(cyclopentadienyl) zirconium dimethyl-alumoxane catalyst system for solution polymerization of EP and EAODM elastomers. US-A-5,229,478 discloses a slurry polymerization process utilizing similar bis(cyclopentadienyl) zirconium based catalyst systems.

In general terms, it is desirable to produce EAODM elastomers under conditions of increased reactivity of the diene monomer component. The reason for this was explained in the above identified '478 patent in the following manner, which still remains true despite the advances attained in such reference. A major factor affecting production costs and hence the utility of an EAODM is diene monomer cost. The diene is a more expensive monomer material than C₂ or C₃. Further, the reactivity of diene monomers with previously known metallocene catalysts is lower than that of C₂ and C₃. Consequently, to achieve the requisite degree of diene incorporation to produce an EAODM with an acceptably fast cure rate, it has been necessary to use a diene monomer concentration which, expressed as a percentage of the total concentration of monomers present, is in substantial excess compared to the percentage of diene desired to be incorporated into the final EAODM product. Since substantial amounts of unreacted diene monomer must be recovered from the polymerization reactor effluent for recycle the cost of production is increased unnecessarily.

Further adding to the cost of producing an EAODM is the fact that, generally, the exposure of an olefin polymerization catalyst to a diene, especially the high concentrations of diene monomer required to produce the requisite level of diene incorporation in the final EAODM product, often reduces the rate or activity at which the catalyst will cause polymerization of ethylene and propylene monomers to proceed. Correspondingly, lower

throughputs and longer reaction times have been required, compared to the production of an ethylene-propylene copolymer elastomer or other α -olefin copolymer elastomer.

The catalyst systems used in the process of the present invention advantageously allow for increased diene reactivity thereby preparing EAODM polymers in high yield and productivity.

5 Additionally, the process of the present invention achieves economical production of EAODM polymers with diene contents of from greater than zero up to 20 weight percent (wt%) or higher, preferably from 0.3 to 20 wt%, more preferably from 0.5 to 12 wt%. These EAODM polymers possess highly desirable fast cure rates.

10 The preferred EAODM elastomers have a C_2 content of from 20 up to 90 wt%, more preferably 30 to 85 wt%, and most preferably 35 to 80 wt%.

The α -olefin, other than C_2 , is generally incorporated into the EAODM polymer at 10 to 80 wt%, more preferably at 20 to 65 wt%. The non-conjugated dienes are generally incorporated into the EAODM polymer at 0.5 to 25 wt%, preferably at 1 to 15 wt%, and more preferably at 3 to 12 wt%. If desired, more than one diene may be incorporated simultaneously, 15 for example 1,4-hexadiene and ENB, with total diene incorporation within the limits specified above.

The catalyst system used in the process of the present invention may be prepared as a homogeneous catalyst by adding the requisite components to a solvent in which polymerization will be carried out by solution polymerization procedures. The catalyst system may also be 20 prepared and employed as a heterogeneous catalyst by adsorbing the requisite components on a catalyst support material such as silica gel, alumina or other suitable inorganic support material. When prepared in heterogeneous or supported form, it is preferred to use silica as the support material. The heterogeneous form of the catalyst system is employed in a slurry polymerization. As a practical limitation, slurry polymerization takes place in liquid diluents in 25 which the polymer product is substantially insoluble. Preferably, the diluent for slurry polymerization is one or more C_{1-5} hydrocarbons. If desired, saturated hydrocarbons such as ethane, propane or butane may be used in whole or part as the diluent. Likewise the α -olefin monomer or a mixture of different α -olefin monomers may be used in whole or part as the diluent. Most preferably the diluent comprises in at least major part the α -olefin monomer or 30 monomers to be polymerized.

The EAODM polymers of the present invention may, as noted above, also be prepared by gas phase polymerization, another well known process wherein reactor cooling typically occurs via evaporative cooling of a volatile material such as a recycle gas, an inert liquid or a monomer or diene that is used to prepare the EAODM polymer. A suitable inert liquid is a C_{3-8} , 35 preferably a C_{4-6} , saturated hydrocarbon monomer. The volatile material or liquid evaporates in

the hot fluidized bed to form a gas that mixes with the fluidizing gas. This type of process is described, for example in EP 89691; US-A-4,543,399; WO 94/25495; WO 94/28032; and US-A-5,352,749, the teachings of which are hereby incorporated by reference. Other relevant teachings, also incorporated by reference, are found in US-A-4,588,790; US-A-4,543,399; US-A-5,352,749; US-A-5,436,304; US-A-5,405,922; US-A-5,462,999; US-A-5,461,123; US-A-5,453,471; US-A-5,032,562; US-A-5,028,670; US-A-5,473,028; US-A-5,106,804; US-A-5,541,270; EP-A-659,773; EP-A-692,500; and PCT Applications WO 94/29032, WO 94/25497, WO 94/25495, WO 94/28032; WO 95/13305; WO 94/26793; and WO 95/07942.

The polymerization reaction occurring in the gas fluidized bed is catalyzed by the continuous or semi-continuous addition of catalyst. Such catalyst can be supported on an inorganic or organic support material.

The gas phase processes suitable for the practice of this invention are preferably continuous processes that provide for a continuous supply of reactants to the reaction zone of the reactor and the removal of products from the reaction zone of the reactor, thereby providing a steady-state environment on the macro scale in the reaction zone of the reactor.

In contrast, solution polymerization conditions use a solvent for the respective components of the reaction. Preferred solvents include mineral oils and the various hydrocarbons that are liquid at reaction temperatures. Illustrative examples of useful solvents include alkanes such as pentane, iso-pentane, hexane, heptane, octane and nonane, as well as mixtures of alkanes including kerosene and Isopar E™, available from Exxon Chemicals Inc.; cycloalkanes such as cyclopentane and cyclohexane; and aromatics such as benzene, toluene, xylenes, ethylbenzene and diethylbenzene.

At all times, the individual ingredients as well as the recovered catalyst components should be protected from oxygen and moisture. Therefore, the catalyst components and catalysts should be, and preferably are, prepared and recovered in an oxygen and moisture free atmosphere. Preferably, therefore, the reactions are performed in the presence of an dry, inert gas such as, for example, nitrogen.

Ethylene is added to a reaction vessel in an amount sufficient to maintain a differential pressure in excess of the combined vapor pressure of the α -olefin and diene monomers. The C_2 content of the polymer is determined by the ratio of C_2 differential pressure to the total reactor pressure. Generally, polymerization occurs with a differential pressure of C_2 of from 10 to 1000 pounds per square inch (psi) (70 to 7000 kPa), most preferably from 40 to 400 psi (30 to 300 kPa). The polymerization temperature is suitably from 25 to 200 °C, preferably from 65 to 170 °C, and most preferably from greater than 75 to 140 °C.

Polymerization may occur in either a batch or a continuous polymerization process. A continuous process is preferred, in which event catalyst, ethylene, α -olefin, diene and optional solvent are continuously supplied to the reaction zone and polymer product continuously removed therefrom.

5 Without limiting in any way the scope of the invention, one means for carrying out such a polymerization process is as follows: In a stirred-tank reactor, α -olefin monomer is introduced continuously together with solvent, diene monomer and C_2 monomer. The reactor contains a liquid phase composed substantially of C_2 , C_3 and diene monomers together with any solvent or additional diluent. If desired, a small amount of a "H"-branch inducing diene such as
10 norbornadiene, 1,7-octadiene or 1,9-decadiene may also be added. Catalyst and cocatalyst are continuously introduced in the reactor liquid phase. The reactor temperature and pressure may be controlled by adjusting the solvent/monomer ratio, the catalyst addition rate, as well as by cooling or heating coils, jackets or both. The polymerization rate is controlled by the rate of catalyst addition. The ethylene content of the polymer product is determined by the amounts of
15 ethylene, α -olefin and diene in the reactor, which are controlled by manipulating the respective feed rates of these components to the reactor. The polymer product molecular weight is controlled, optionally, by controlling other polymerization variables such as the temperature, monomer concentration, or by a stream of hydrogen introduced to the reactor, as is well known in the art. The reactor effluent is contacted with a catalyst kill agent such as water. The
20 polymer solution is optionally heated, and the polymer product is recovered by flashing off gaseous ethylene and propylene as well as residual diene and residual solvent or diluent at reduced pressure, and, if necessary, conducting further devolatilization in equipment such as a devolatilizing extruder. In a continuous process, the mean residence time of the catalyst and polymer in the reactor generally is from 5 minutes to 8 hours, and preferably from 10 minutes to
25 6 hours.

In a preferred manner of operation, the polymerization is conducted in a continuous solution polymerization system comprising two reactors connected in series or parallel. In one reactor, a relatively high molecular weight product (M_w from 300,000 to 600,000, more preferably 325,000 to 500,000) is formed while, in the second reactor, a product of a relatively
30 low molecular weight (M_w 50,000 to 300,000) is formed. As an alternative, the same molecular weight product can be produced in each of the two reactors. The final product is a blend of the two reactor effluents that are combined prior to devolatilization to result in a uniform blend of the two polymer products. Such a dual reactor process allows for the preparation of products having improved properties. In a preferred embodiment, the reactors are connected in series,
35 that is effluent from the first reactor is charged to the second reactor and fresh monomer, solvent and hydrogen are added to the second reactor. Reactor conditions are adjusted such

that the weight ratio of polymer produced in the first reactor to that produced in the second reactor is from 20:80 to 80:20. If desired, however, a broader range of weight ratios may be used. In addition, the temperature of the second reactor is controlled to produce the lower M_w product. This system beneficially allow for production of EAODM products having a large MV range, as well as excellent strength and processability. Preferably the MV of the resulting product is adjusted to fall in the range from 1 to 150, more preferably from 10 to 120 and most preferably from 15 to 100. Although this preferred manner of operation employs two reactors, three or more reactors may also be used.

Examples

10 The following examples illustrate but do not, either explicitly or by implication, limit the present invention. Unless otherwise stated, all parts and percentages are expressed on a weight basis. Examples of the present invention are identified by Arabic numerals and comparative examples are represented by letters of the alphabet.

15 For catalyst examples, ^1H and ^{13}C NMR spectra are recorded on a Varian XL (300 MHz) spectrometer. Chemical shifts are determined relative to TMS (tetramethylsilane) or through residual CHCl_3 in CDCl_3 or residual C_6HD_5 in C_6D_6 , relative to TMS. Tetrahydrofuran (THF), diethylether, toluene, and hexane are used following passage through double columns charged with activated alumina and alumina supported mixed metal oxide catalyst (Q-5[®] catalyst, available from Engelhard Corp.) The compounds n-BuLi, KH, all Grignard reagents, 20 and 1,4-diphenyl-1,3-butadiene are all used as purchased from Aldrich Chemical Company. All catalyst syntheses are performed under dry nitrogen atmosphere using a combination of glove box and high vacuum techniques.

25 Polymer example preparation employs either a continuous process or a batch process. With a batch process, monomers and other specified components are added to a reactor apparatus before starting the process. For a continuous process, monomers are added to a reactor apparatus as needed, with flow rate variation being used to alter monomer concentrations. Each example specifies the process type and conditions. Process run times of one to two hours generally suffice to allow the reaction to reach an equilibrium and provide representative polymer samples for analysis.

30 Physical property evaluation of EAODM polymers uses a number of standard tests: MV; compositional analysis via Fourier transform infrared analysis (FTIR) (ASTM D3900); and density (ASTM D-792). Other definitive properties include B value, determined as previously described, rheology ratio, determined as described below, and reactivity ratio product, also determined as described below.

Rheology ratio ($V_{0.1}/V_{100}$) is determined by examining samples using melt rheology techniques on a Rheometric Scientific, Inc. ARES (Advanced Rheometric Expansion System) dynamic mechanical spectrometer (DMS). The samples are examined at 190°C using the dynamic frequency mode and 25 mm diameter parallel plate fixtures with a 2 mm gap. With a strain rate of 8% and an oscillatory rate that is incrementally increased from 0.1 to 100 radians per second (rad/s), 5 data points taken for each decade of frequency analyzed. Each sample (either pellets or bale) is compression molded into 3 inch (1.18 centimeter (cm)) plaques 1/8 inch (0.049 cm) thick at 20,000 psi (137.9 megapascals (MPa)) pressure for 1 minute at 180°C. The plaques are quenched and cooled (over a period of 1 minute) to room temperature. A 25 mm plaque is cut from the center portion of the larger plaque. These 25mm diameter aliquots are then inserted into the ARES at 190°C and allowed to equilibrate for 5 minutes prior to initiation of testing. The samples are maintained in a nitrogen environment throughout the analyses to minimize oxidative degradation. Data reduction and manipulation are accomplished by the ARES2/A5:RSI Orchestrator Windows 95 based software package. The $V_{0.1}/V_{100}$ ratio (rheology ratio or "RR") measures the slope of the viscosity versus shear rate curve.

Reactivity ratios, r_1 and r_2 , are calculated from the diad and triad distributions in the ^{13}C NMR spectrum based on a terminal copolymerization model, and the reactivity ratio product (RRP) is then obtained by multiplying these two values (r_1 and r_2). ^{13}C NMR sample preparation is as detailed above.

Polymer crystallinity is determined by differential scanning calorimetry (DSC) using a TA DSC-2920 equipped with a liquid nitrogen cooling accessory. Samples are prepared as thin films and placed in aluminum pans. They are heated initially to 180°C and maintained at this temperature for four minutes to ensure substantially complete melting. They are then cooled at 10°C per minute to -100°C before being reheated to 150°C at 10°C per minute. The T_g is obtained from the melting point curve using the first derivative of temperature. The total heat of fusion is obtained from the area under the melting curve. The percent crystallinity is determined by dividing the total heat of fusion by the heat of fusion value for polyethylene (292 joules per gram (J/g)).

Catalyst efficiency (Cat. Eff.) is specified in terms of million pounds of polymer per pound of Group IV metal in the catalyst (MM#/#). For the batch process, it is determined by weighing the polymer product and dividing by the amount of Group IV metal added to the reactor. For a continuous process, polymer product weight is determined by measured ethylene or vent conversion.

Examples of EAODM polymers that represent the present invention employ a catalyst prepared as described below whereas comparative example EAODM polymers are prepared

using a constrained geometry catalyst such as described in US-A-5,491,246; US-A-5,486,632; and US-A-5,470,993.

Catalyst Preparation

Example 1 - Synthesis of (t-butylamido)-dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (IV)

5 dimethyl

1a) Preparation of 5,6,7-tetrahydro-2-methyl-s-indacen-1-one

Indan (59.0876 grams (g), 0.5000 moles) and 2-bromoisobutyryl bromide (114.9493 g, 0.5000 moles) are stirred in CH_2Cl_2 (500 milliliters (mL)) at 0°C as AlCl_3 (201.36 g, 1.5101 moles) is added slowly as a solid under a nitrogen (N_2) flow. This mixture is then stirred for 6
10 hours at 20 - 25°C . After the reaction period the mixture is poured over ice and allowed to sit 16 hours. The mixture is then decanted into a separatory funnel and the remaining salts are washed well with CH_2Cl_2 . The organic layer is then separated and the volatiles removed resulting in isolation of a dark oil. Vacuum distillation results in isolation of the desired product as a yellow oil (82.43g, 88.5 % yield).

15 1b) Preparation of s-Indacen-1,2,3,5-tetrahydro-6-methyl

Example 1a) product (40.00 g, 0.2148 moles) is stirred in diethylether (150 mL) at 0°C under nitrogen as NaBH_4 (8.12 g, 0.2148 moles) and EtOH (100 mL) are added slowly to provide a mixture that is then stirred and allowed to react for 16 hours at 20 - 25°C . After this
20 period, the mixture is poured on ice and then acidified using an aqueous 1 Molar (M) HCl solution. The organic fraction is then washed with 1 M HCl (2 x 100 mL). The volatiles are then removed from the solution and the residue redissolved in benzene and refluxed with p-toluensulphonic acid (0.11 g) using a Dean-Stark apparatus for 5 hours. The mixture is then extracted using 1 M NaHCO_3 (2 x 100 mL). The organic layer is separated and the volatiles removed resulting in isolation of the desired product as a white crystalline solid (28.36 g, 77.6 %
25 yield).

1c) Preparation of (1,5,6,7-tetrahydro-2-methyl-s-indacen-1-yl) lithium

Example 1b) product (25.000 g, 0.14684 moles) is stirred in hexane (400 mL) as nBuLi (0.17621 moles, 70.48 mL of 2.5 M solution in hexane) is added slowly to provide a reaction mixture that is then stirred and allowed to react for 16 hours during which time a solid
30 precipitates. The mixture is then filtered to isolate the desired product as a pale yellow solid that is used without further purification or analysis (24.3690 g, 94.2 % yield).

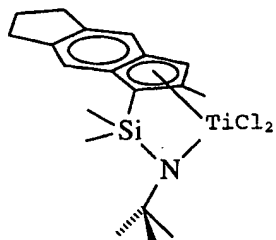
1d) Preparation of N-(1,1-dimethylethyl)-1,1-dimethyl-1-(1,5,6,7-tetrahydro-2-methyl-s-indacen-1-yl)silamine

Example 1c) product (25.0 g, 0.1419 moles) in tetrahydrofuran (THF) (200 mL) is added dropwise to a solution of dimethylsilyl(t-butylamino)chloride (23.518 g, 0.1419 moles) in THF (250 mL) over a 1 hour period of time to provide a reaction mixture that is then stirred and allowed to react for 20 hours. After this period, volatiles are removed and the residue extracted and filtered using hexane. Removal of the hexane results in isolation of the desired product as a red-yellow oil (37.55 g, 88.0% yield).

1e) Preparation of dilithio N-(1,1-dimethylethyl)-1,1-dimethyl-1-(1,5,6,7-tetrahydro-2-methyl-s-indacen-1-yl)silanamide

Example 1d) product (8.00 g, 0.2671 moles) is stirred in hexane (110 mL) as nBuLi (0.05876 moles, 23.5 mL of 2.5 M solution in hexane) is added dropwise to provide a reaction mixture that is then stirred and allowed to react for 16 hours. After this period, the desired product is isolated as a light yellow solid via filtration that is used without further purification or analysis (6.22 g, 75% yield).

1f) Preparation of dichloro[N-(1,1-dimethylethyl)-1,1-dimethyl-[1,2,3,4,5-η)-1,5,6,7-tetrahydro-2-methyl-s-indacen-1-yl]silanamido(2-)-N] titanium



Example 1e) product (4.504 g, 0.01446 moles) in THF (40 mL) is added dropwise to a slurry of $\text{TiCl}_3(\text{THF})_3$ (5.359 g, 0.001446 moles) in THF (100 mL) that is stirred for 1 hour before adding PbCl_2 (2.614 g, 0.000940 moles) with continued stirring for an additional hour. After this period, the volatiles are removed and the residue extracted and filtered using toluene. Removal of the toluene results in isolation of a dark residue. This residue is slurried in hexane and the desired product is then isolated via filtration as a red solid (3.94 g, 65.0% yield).

1g) Synthesis of the complex of Formula IV

Example 1f) product (0.450 g, 0.00108 moles) is stirred in diethylether (30 mL) as MeMgBr (0.00324 moles, 1.08 mL of 3.0t M solution in diethylether) is added slowly to provide a reaction mixture that is then stirred and allowed to react for 30 minutes. After this period, the

volatiles are removed and the residue extracted and filtered using hexane. Removal of the hexane results in isolation of the desired product as a solid (0.37 g, 90.6% yield).

Example 2 - Synthesis of the complex of Formula III

In a drybox (glovebox), (t-butylamido)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium dichloride (Example 1 f) (0.300 grams, 0.72 mmol) is suspended in 50 mL of cyclohexane in a 100 mL round bottom flask. Ten equivalents of a mixture of isomers of 2,4-hexadiene (0.822 mL, 7.21 mmol) are added to the contents of the flask to form a mixture. Two and a quarter equivalents of a 2.0 M Et₂O solution of n-BuMgCl (0.81 mL, 1.62 mmol) are added to the mixture to form a reaction mixture. The flask is fitted with a condenser and the reaction mixture is heated to reflux for one hour. Upon cooling, volatiles are removed under reduced pressure to leave a residue that is then extracted with hexane and filtered through a diatomaceous earth filter aid on a 10-15 mm glass frit. The hexane is removed under reduced pressure to afford 0.29 grams (g) of a brown oily solid as a desired product (equivalent to a 94% yield). The product, as characterized by ¹H and ¹³C NMR, is (t-butylamido)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene.

Example 3 - Synthesis of the complex of Formula VII and VIII

Using the apparatus and procedure of Example 2, save for substituting 15 equivalents of a mixture of isomers of 1,3-pentadiene (1.08 mL, 10.81 mmol) for the 10 equivalents of the mixture of hexadiene isomers, two equivalents of a 2.5 M hexane solution of n-BuLi (0.58 mL, 1.44 mmol) for the 2.25 equivalents of the 2.0 M Et₂O solution of n-BuMgCl and increasing the reflux time to three hours, 0.257g of a brown oily solid (86% yield). The solid, as characterized by ¹H and ¹³C NMR, is (t-butylamido)-dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium(II) 1,3-pentadiene. The product is isolated as a mixture of two geometrical isomers resulting from the orientation of 1,3-pentadiene with respect to the methyl group on the indacenyl ring as shown in Formulae VII and VIII.

Examples 4-7 and Comparative Examples A and B

Five sample ethylene/propylene/ENB terpolymer compositions, four representing this invention (Examples 4-7) and one being a comparative example (Comparative Example A), are prepared using the same basic procedure with certain modifications as indicated in Tables IA-1C in a 3.8 liter (L) stirred reactor designed for continuous addition of reactants and continuous removal of polymer solution, devolatilization and polymer recovery.. Examples 4-7 are prepared using the catalyst of Example 1. Comparative Example A is prepared using (tetramethylcyclopentadienyl)dimethyl(t-butylamido)silanetitanium 1,3-pentadiene as the catalyst. The co-catalyst for all five samples is FAB. The scavenging compound for Examples 4-5 and Comparative Example A is MMAO (triisobutyl aluminum modified methylalumoxane). The

scavenging compounds for Examples 6 and 7 are, respectively, DIEL-N ((diisopropylamido)diethylaluminum) and DIBAL-NS ((bistrimethylsilylamido)diisobutylaluminum). The ratio of moles of FAB to moles of titanium (Ti) is 3.0 for Examples 4-7 and 3.6 for Comparative Example A. The melt index (MI) for Comparative Example A is 25.0 g/10 minutes. MI is used for Comparative Example A because it has a M_w that is too low to measure a MV. Examples 4-7 have a sufficiently high M_w to measure a MV.

A further comparative example (B) is produced in a similar manner, but without hydrogen. The composition of this polymer is similar to that of Examples 4-7, and the removal of hydrogen permits production of a polymer with a closer match on molecular weight.

Referring to Figure 1, ethylene (4), propylene (5), and hydrogen (6) are combined into one stream (16) before being introduced into a diluent mixture (3) comprising a mixed alkane solvent (Isopar-E™, available from Exxon Chemicals Inc.) (1) and diene (2) to form a combined feed mixture (7) that is continuously injected into the reactor (10). The catalyst (8) and a blend of the cocatalyst and scavenging compound (9) are combined into a single stream (17), also continuously injected into the reactor.

Table IA shows flow rates for solvent, ethylene (C_2) and propylene (C_3) in pounds per hour (pph). Table IA also shows the percent conversion of C_2 and polymer production rate (in pph). Table IB shows concentrations of catalyst (Cat), cocatalyst (Cocat) and scavenger (Scav) in parts per million parts of Al (ppm). Table IB also shows a ratio of cocat to metal (M), where M is titanium (Ti), and flow rates, in pph, for Cat, Cocat and Scav. Table IC shows Reactor Temperature (Temp) in °C, hydrogen flow, in standard cubic centimeters per minute (sccm), ENB flow rate (pph), a ratio of scavenger:titanium (Scav/Ti) and polymer properties (MV, MI, and EAODM composition (as determined by FTIR)), B Value, $V_{0.1}/V_{100}$ and RRP.

A reactor exit stream (15) is continuously introduced into a separator (11), where molten polymer is continuously separated from the unreacted comonomer, unreacted ethylene, unreacted hydrogen, unreacted ENB, and solvent (14). The molten polymer is subsequently strand chopped or pelletized and, after being cooled in a water bath or pelletizer (12), the solid pellets are collected (13).

Table IA

| Ex No | Solvent Flow (pph) | C ₂ Flow (pph) | C ₃ Flow (pph) | C ₂ Conv % | Reactor Pressure (psig/MPa) | Polymer production rate (pph) |
|-------|--------------------|---------------------------|---------------------------|-----------------------|-----------------------------|-------------------------------|
| 4 | 37.5 | 2.4 | 3.6 | 75.1 | 475.2/3.28 | 4.0 |
| 5 | 38.0 | 2.4 | 3.6 | 76.7 | 474.9/3.27 | 4.1 |
| 6 | 36.6 | 2.4 | 3.6 | 77.2 | 475.4/3.28 | 4.1 |
| 7 | 37.0 | 2.4 | 3.6 | 75.9 | 475.2/3.28 | 4.0 |
| A | 35.1 | 2.4 | 3.6 | 77.0 | 474.9/3.27 | 4.3 |
| B | 36.9 | 2.4 | 3.6 | 74.6 | 474.9/3.27 | 4.06 |

Table IB

| Ex No | Cat Conc (ppm) | Cocat Conc (ppm) | Scav Conc (ppm) | Cocat/Ti Ratio | Cat flow (pph) | Cocat flow (pph) | Scavenger flow (pph) |
|-------|----------------|------------------|-----------------|----------------|----------------|------------------|----------------------|
| 4 | 12.3 | 348.3 | 42.7 | 3.0 | 0.152 | 0.172 | 0.150 |
| 5 | 12.3 | 348.3 | 42.7 | 3.0 | 0.094 | 0.106 | .090 |
| 6 | 3.3 | 76.4 | 6.4 | 3.0 | 0.541 | 0.750 | 0.310 |
| 7 | 3.3 | 76.4 | 12.5 | 3.0 | 0.319 | 0.442 | 0.475 |
| A | 6.6 | 198.1 | 21.1 | 3.6 | 0.742 | 0.949 | 1.240 |
| B | 6.6 | 198.2 | 21.4 | 3.6 | 0.285 | 0.365 | 0.477 |

Table IC

| Ex No | Reac- tor Temp (°C) | H ₂ Flow (sccm) | ENB Flow (pph) | Cat Eff (MM#/#) | Scav/ Ti Ratio | B Value | V _{0.1} /V ₁₀₀ | MV | RRP | C ₂ (wt%) | C ₃ (wt%) | ENB (wt %) | MW (M _w) | MWD |
|-------|------------------------------|----------------------------------|----------------------|--------------------|----------------------|------------|------------------------------------|------|------|-------------------------|-------------------------|------------------|-------------------------|------|
| 4 | 90.7 | 25.9 | 0.70 | 2.16 | 6.1 | 0.95 | 13.8 | 29.6 | 1.24 | 44.3 | 48.2 | 7.5 | 132500 | 1.98 |
| 5 | 90.9 | 25.9 | 0.40 | 3.58 | 5.9 | -- | | 24.4 | -- | 44.0 | 51.5 | 4.5 | 123200 | 1.96 |
| 6 | 90.5 | 26.0 | 0.40 | 2.29 | 2.0 | -- | 11.3 | 26.3 | -- | 44.7 | 50.8 | 4.6 | 121100 | 2.51 |
| 7 | 89.6 | 26.0 | 0.40 | 3.84 | 10.0 | 1.0 | 13.4 | 31.6 | 1.23 | 44.6 | 51.0 | 4.5 | 139700 | 2.03 |
| A | 90.8 | 25.9 | 0.70 | 0.87 | 9.5 | 0.90 | | 1.3 | 1.55 | 44.1 | 51.4 | 4.5 | 51300 | 1.85 |
| B | 90.8 | 0.0 | 0.70 | 2.16 | 9.6 | -- | 10.5 | 18.6 | -- | 43.4 | 51.4 | 5.2 | 101800 | 2.08 |

-- means not measured

The data presented in Table IC illustrate several points. First, under essentially the same reaction conditions, the M_w of the Example 4-7 polymers are an order of magnitude greater than that of Comparative example A as exemplified by MV measurements. This M_w increase is not dramatically affected by the type of scavenger used in the reaction. Second, at equal ENB flow rates (Example 4 and comparative example A) there is a 66.7% increase in ENB incorporation into the polymer. In order to obtain an ENB concentration like that of Comparative Example A, the ENB flow rate must be reduced from 0.7 pph to 0.4 pph for Examples 5-7. A comparison of Comparative Example A with Example 5 shows a dramatically improved catalyst efficiency in producing essentially the same polymer from an ENB incorporation point of view.

The data in Table IC also suggest that the polymers of the present invention, as represented by Examples 4-7, have desirable shear thinning behavior and a satisfactory level of long chain branching. The $V_{0.1}/V_{100}$ ratio (rheology ratio) is a means of measuring the slope of a viscosity versus shear rate curve. A high $V_{0.1}/V_{100}$ ratio, like that of examples 4-7, suggests greater shear sensitivity or shear thinning relative to a low $V_{0.1}/V_{100}$ ratio, like that of Comparative Example B. As shear thinning is typically affected by both MWD and level of long chain branching and as the polymers of Examples 4-7 and Comparative Examples A and B all have similar molecular weight distributions (MWD), a higher $V_{0.1}/V_{100}$ ratio also indicates more long chain branching. Polymers of this invention have a higher rheology ratio at the same MV as comparative polymers as evidenced by comparing Examples 4-7 with Comparative Example B. Comparative Example B, prepared in the absence of hydrogen, has a lower $V_{0.1}/V_{100}$ ratio than any of Examples 4-7. As the lack of hydrogen generally results in a higher level of vinyl unsaturation and hence enhanced long chain branching and higher shear thinning behavior and higher $V_{0.1}/V_{100}$ ratio, the data suggest that hydrogen need not be excluded from the process of the present invention.

Example 8.

Terpolymerization of ethylene, propylene, and ENB is carried out using a 3.8 L stainless steel reactor charged with 1448 g of Isopar E™ (mixed alkanes, available from Exxon Chemicals, Inc.), 230.3 g of propylene, 32.9 g of ENB, and 13.8 millimoles (mMol) of hydrogen. The reactor is heated to 100°C and then saturated with ethylene to 460 psig (3.24 MPa). The catalyst is prepared in a dry box by syringing together 1.0 micromol (0.005 M solution) of the Example 1 catalyst, 1.5 micromol (0.0075 M solution) of FAB as the cocatalyst, 10.0 micromol (0.050 M solution) of (diisopropylamido)diethylaluminum as the scavenger, and sufficient Isopar E™ to give a total volume of 18 mL. The catalyst solution is then transferred via syringe to a catalyst addition loop and injected into the reactor over approximately 4 minutes using a flow of high pressure solvent. Polymerization is allowed to proceed for 10 minutes while feeding

ethylene on demand to maintain a pressure of 460 psig (3.24 MPa). The amount of ethylene consumed during the reaction is monitored using a mass flow meter. The polymer solution is then poured from the reactor into a nitrogen-purged glass kettle and about 2000 parts per million parts of polymer (ppm) of stabilizer (Irgafos 186™ and Irganox™ 1076) is added and
 5 mixed well with the polymer solution. The stabilized polymer solution is poured into a tray, air dried overnight, and then thoroughly dried in a vacuum oven set at a temperature of 120°C for one day.

The yield of terpolymer is 89.7 g, and the Cat. Eff. is 1.9 million. The terpolymer has a C₂/C₃ weight ratio of 2.1 (64.5 wt% C₂, 30.1 wt% C₃), and an ENB content of 5.5 wt%. The MV
 10 is 84.4 and the molecular weight (M_w) is 185,500 with a MWD (M_w/M_n) of 2.04. The B value is 0.96 and the RRP for ethylene/ propylene is 1.16. The terpolymer has a T_g of -44.9°C and crystallinity of 4.2%.

Example 9

Using the apparatus, catalyst and procedure of Example 8, an ethylene/propylene/ENB
 15 terpolymer is prepared by charging the reactor with 1457 g of Isopar E™, 232.4 g of propylene, 33.8 g of ENB, and 13.8 mMol of hydrogen. The terpolymer yield is 104.7 g, and the Cat. Eff. is 2.2 million. The terpolymer has a weight ratio of ethylene to propylene of 2.0 (65.4 wt% ethylene, 32.1 wt% propylene), and an ENB content of 2.5 wt%. The MV is 33.0 and the M_w is 134,300 with a MWD of 1.78. The B value is 0.94 and the RRP for ethylene/ propylene is 1.21.
 20 The terpolymer has a T_g of -46.9°C and a crystallinity of 6.2%.

Comparative Example C (C05R03)

Using the apparatus and procedure of Examples 4-7 and Comparative examples A and B and (tetramethylcyclopentadienyl)dimethyl(t-butylamido)silane/titanium dimethyl as the catalyst, FAB as the co-catalyst and MMAO as a scavenging compound, an
 25 ethylene/propylene/ENB terpolymer is prepared by flowing into the reactor the amounts shown in the following tables. The Al/Ti ratio is 6:1, the MMAO flow rate is 0.3 pph and the MMAO concentration is 24.91 ppm, based on _____. As in Comparative Example B, there is no hydrogen flow. Tables IIA and IIB show polymerization parameters and properties of the resultant polymer.

Table IIA

| Ex No | Solvent Flow (pph) | C ₂ Flow (pph) | C ₃ Flow (pph) | Solvent/C ₂ ratio | C ₂ Conv % | Reactor Pressure (psig/MPa) | Polymer production rate (pph) | Cat Conc (ppm) | Cocat Conc (ppm) | Cocat/Ti Ratio | Cat flow (pph) |
|-------|--------------------|---------------------------|---------------------------|------------------------------|-----------------------|-----------------------------|-------------------------------|----------------|------------------|----------------|----------------|
| C | 39.0 | 3.0 | 1.46 | 10.1 | 70.1 | 475 | 3.88 | 6 | 176.8 | 2.99 | 0.372 |

Table IIB

| Ex No | Reactor Temp (°C) | Cocat Flow (pph) | ENB Flow (pph) | Cat Eff (MM#/#) | B Value | V _{0.1} /V ₁₀₀ | MV | RRP | C ₂ (wt%) | C ₃ (wt%) | ENB (wt%) | M _w | MW D |
|-------|-------------------|------------------|----------------|-----------------|---------|------------------------------------|------|------|----------------------|----------------------|-----------|----------------|------|
| C | 89.5 | 0.404 | 0.53 | 1.76 | 0.93 | 6.7 | 23.0 | 1.47 | 69.6 | 26.9 | 3.4 | 112,800 | 1.83 |

The data in Table IIB, like that presented in Table IC for Comparative Example B, demonstrate that polymers produced in accordance with the present invention, even if made from the same starting materials and under the same conditions, but with a different catalyst, clearly differ from those made with the latter catalyst.

Example 10

Using the apparatus and procedure of Example 8 and the catalyst of Example 2, an ethylene/butene-1/ENB terpolymer is prepared by charging the reactor with 1455 g of Isopar E™, 303.3 g of butene-1, 42.6 g of ENB, and 9.46 mMol of hydrogen.

The terpolymer yield is 83.0 g, and the Cat. Eff. is 1.2 million. The resulting elastomer had a MW of 168,700, a MWD of 2.02, a MI of 1.7 g/10 min and a crystallinity of 13%.

Comparative Example D

Using the apparatus and procedure of Example 8 and a different catalyst, an ethylene/butene-1/ENB terpolymer is prepared by charging the reactor with 1443 g of Isopar E™, 304.7 g of butene-1, 90.9 g of ENB, and 9.5 mMol of hydrogen. The catalyst is prepared in a dry box by syringing together 2.0 micromol (0.005 M solution) of the metal complex (tetramethylcyclopentadienyl)dimethyl (t-butylamido)-silanetitanium (II) 1,3-pentadiene, 6.0 micromol (0.015 M solution) of the Example 8 cocatalyst, 50.0 micromol (0.125 M solution) of the Example 8 scavenger, and sufficient Isopar E™ to give a total volume of 18 mL. The catalyst solution is then transferred into the reactor as in Example 8. The terpolymer yield is 157.7 g, and the Cat. Eff. is 1.6 million. The terpolymer has a MW of 46,700, MWD of 1.97 a MI of 201.7 and a crystallinity of 10.5%.

The difference in MW between the terpolymers of Example 10 and Comparative Example D significantly affects polymer properties such as Tensile at Break (ASTM D1708) and Percent Elongation at Break (ASTM D1708) Example 10 has a Tensile at Break of 1150 psi (8.90 MPa) as opposed to 375 psi (2.64 MPa) for Comparative Example C, and an Percent Elongation at Break of 840 as opposed to 567 for Comparative Example C. This data evidence the effect of changing catalysts upon resulting polymers.

Examples 11-13 and Comparative Example E

Using the apparatus and procedure of Example 8, and the catalyst of Example 1 for Examples 11, 13 and 14, the catalyst of Example 2 for Example 12 and the catalyst of Comparative Example A for Comparative Example E, and varying cocatalysts, four ethylene/propylene/ENB terpolymers are prepared using the ingredient amounts shown in Table

IIIA. The cocatalyst for Example 12 and Comparative Example E is FAB. The cocatalyst for Examples 11, 13 and 14 is di(hydrogenated-tallowalkyl)methylammonium tetrakis(pentafluorophenyl)borate. Polymerization results are shown in Table IIIB. The scavenger for Examples 11, 13 and 14 is (diisopropylamido)diethylaluminum. The scavenger
5 for Example 12 is DIBAL-NS and for Comparative Example E is a MMAO

Table IIIA

| Ex No | Sol-vent mass (g) | C3 Load (g) | ENB Load (g) | H ₂ (mmol) | Catalyst (micro-moles) | Catalyst (molarity) | CoCat (micro-moles) | CoCat (molarity) | Scavenger (micro-moles) | Scavenger (molarity) | Polymer Mass |
|-------|-------------------|-------------|--------------|-----------------------|------------------------|---------------------|---------------------|------------------|-------------------------|----------------------|--------------|
| 11 | 1449.7 | 305.8 | 90 | 3.6 | 2.5 | 0.005 | 3.75 | 0.0075 | 62.5 | 0.05 | 60 |
| 12 | 1447.7 | 206.4 | 40 | 9.84 | 1.52 | 0.005 | 4.5 | 0.015? | 37.5 | 0.05 | 130.7 |
| 13 | 1460.5 | 205.7 | 39.5 | 6.86 | 1 | 0.005 | 1.5 | 0.0075 | 10 | 0.05 | 71 |
| E | 1467 | 307.6 | 90 | 3.65 | 2 | 0.005 | 6 | 0.015 | 20 | 0.05 | 203.4 |
| 14 | 1461.0 | 205.8 | 36.5 | 13.8 | 1.5 | 0.005 | 2.25 | 0.0075 | 7.5 | 0.05 | 93.8 |

Table IIIB

| Ex No | Cat Eff | B Value | RRP | C ₂ H ₄ (wt%) | C ₃ H ₆ (wt%) | ENB (wt%) | MV | M _w | MWD | Tg (°C) | % Crys- tallinity |
|-------|---------|---------|------|--|--|--------------|-------|----------------|------|---------|----------------------|
| 11 | 0.37 | -- | -- | 55.4 | 32.3 | 12.4 | 122.2 | 277,600 | 1.99 | -42.1 | 0.0 |
| 12 | 1.36 | -- | -- | 67.2 | 26.2 | 6.6 | 69.6 | 176900 | 1.82 | -36.5 | 7.0 |
| 13 | 1.48 | -- | -- | 66.0 | 27.0 | 6.8 | 138.1 | 264,800 | 1.98 | -42.5 | 4.8 |
| E | 2.12 | -- | -- | 49.1 | 45.5 | 5.5 | 13.9 | 95,200 | 1.90 | -47.5 | 14.7 |
| 14 | 1.31 | 0.95 | 1.22 | 62.4 | 31.6 | 6.1 | 69.0 | 158,400 | 2.05 | -47.3 | 6.5 |

-- means not measured

DW00013

The data in Table IIIB demonstrate that use of a preferred catalyst in the process of the present invention yields polymers having a greater ENB content, a higher M_w or both relative to polymers produced under the same conditions, but with another catalyst.

Example 15

- 5 Using the catalyst of Example 3, FAB as the cocatalyst, MMAO as the scavenger, and the procedure and apparatus of Example 8, an ethylene/propylene/ENB interpolymers is prepared using the ingredient amounts shown in Table IVA. The interpolymers has properties as shown in Table IVB.

Table IVA

| Ex No | Sol-vent mass (g) | C ₃ Loaded (g) | ENB Loaded (g) | H ₂ (mmol) | Catalyst (micro-moles) | Catalyst (molarity) | CoCat (micro-moles) | CoCat (molarity) | Scavenger (micro-moles) | Scavenger (molarity) | Poly-mer Mass (g) |
|-------|-------------------|---------------------------|----------------|-----------------------|------------------------|---------------------|---------------------|------------------|-------------------------|----------------------|-------------------|
| 15 | 1455.7 | 207.2 | 40.9 | 18.6 | 1.5 | 0.005 | 4.5 | 0.015 | 15 | 0.05 | 135 |

Table IVB

| Ex No | Cat Eff | RRP | C ₂ H ₄ (wt%) | C ₃ H ₆ (wt%) | ENB (wt%) | MV | MW | MWD | Tg (°C) | % Crystallinity |
|-------|---------|-----|-------------------------------------|-------------------------------------|-----------|------|---------|------|---------|-----------------|
| 15 | 0.63 | -- | 66.9 | 26.5 | 6.6 | 95.8 | 220,300 | 1.92 | -45.4 | 7.8 |

-- means not measured

The data in Table IVB show that similar results are obtained with a different preferred catalyst in conjunction with the process of the present invention.

Results similar to those presented in Examples 1-15 are expected with other catalysts, cocatalysts, scavengers and process parameters, all of which are disclosed above.

Claims:

1. A random ethylene/ α -olefin/diene monomer interpolpolymer, the interpolpolymer having (a) a weight ratio of ethylene to α -olefin within a range of from 90:10 to 10:90, the α -olefin being a C₃₋₂₀ α -olefin; (b) a diene monomer content within a range of from greater than 0 to 25 percent by weight, based on interpolpolymer weight; and (c) a B value of from 0.94 to 1.0, the B value being determined by ¹³C NMR spectroscopy and the formula $B = P_{OE}/(2 P_E P_O)$ wherein P_E is a molar fraction of ethylene units derived from ethylene, P_O is a molar fraction of α -olefin units derived from an α -olefin, and P_{OE} is a ratio of the number of α -olefin/ethylene chains to the number of all dyad chains in the interpolpolymer.
2. The interpolpolymer of Claim 1, wherein the alpha-olefin is selected from propylene, butene-1, hexene-1 and octene-1 and the diene monomer is selected from 5-ethylidene-2-norbornene, 5-vinylidene-2-norbornene, 5-methylene-2-norbornene, 1,4-hexadiene, 1,3-pentadiene, dicyclopentadiene, 7-methyl-1,6-octadiene, 1,3-butadiene, 4-methyl-1,3-pentadiene, 5-methyl-1,4-hexadiene, 6-methyl-1,5-heptadiene, norbornadiene, 1,7-octadiene, and 1,9-decadiene.
3. The interpolpolymer of Claim 1, wherein the interpolpolymer has at least one characteristic selected from a rheology ratio ($V_{0.1}/V_{100}$) within a range of from 3 to 90, has a Mooney Viscosity (ML_{1+4} at 125° C) within a range of from 1 to 150, a reactivity ratio product within a range of from 1 to less than 1.25.
4. The interpolpolymer of Claim 1 wherein the interpolpolymer has, relative to a comparative ethylene/ α -olefin/diene monomer interpolpolymer prepared from the same monomers, at the same temperature and with the same conversion using either (tetramethylcyclopentadienyl)-dimethyl(t-butylamido)silanetitanium dimethyl or (tetramethylcyclopentadienyl)dimethyl (t-butylamido)-silanetitanium 1,3-pentadiene as a catalyst, at least one superior characteristic selected from (a) a rheology ratio is at least 10% greater than that of the comparative interpolpolymer, (b) a diene content that is at least 50 percent greater than that of the comparative interpolpolymer, (c) a molecular weight that is at least 1.5 times greater than that of the comparative interpolpolymer, (d) a Mooney Viscosity that is at least 2.5 times greater than that of the comparative interpolpolymer, and (e) glass transition temperature (T_g) that is at least one degree Centigrade lower than that of the comparative polymer with a crystallinity of greater than 0 but less than five percent.
5. A process for preparing the interpolpolymer of any of Claims 1-4, the process comprising contacting ethylene, at least one C₃₋₂₀ α -olefin monomer and a diene monomer with a

catalyst and an activating cocatalyst, the catalyst being a metal complex that corresponds to the formula



5 wherein

M is titanium, zirconium or hafnium in the +2, +3 or +4 formal oxidation state;

A' is a substituted indenyl group substituted in at least the 2 position with a group selected from hydrocarbyl, fluoro-substituted hydrocarbyl, hydrocarbyloxy-substituted hydrocarbyl, dialkylamino- substituted hydrocarbyl, silyl, germyl and mixtures thereof, said group containing up to
10 40 nonhydrogen atoms, and said A' further being covalently bonded to M by means of a divalent Z group;

Z is a divalent moiety bound to both A' and M via σ -bonds, said Z comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

15 X is an anionic or dianionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π -bound ligand groups;

X' independently each occurrence is a neutral Lewis base ligating compound, having up to 20 atoms;

p is 0, 1 or 2, and is two less than the formal oxidation state of M, with the proviso that
20 when X is a dianionic ligand group, p is 1; and

q is 0, 1 or 2.

6. The process of Claim 5, wherein the catalyst is selected from group A that includes (t-butylamido)dimethyl(η^5 -2-methylindenyl)silane-titanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethyl(η^5 -2-methylindenyl)silane-titanium (II) 1,3-pentadiene, (t-butylamido)-
25 dimethyl(η^5 -2-methyl-indenyl)silane-titanium (II) 2,4-hexadiene, (t-butylamido)-dimethyl(η^5 -2-methylindenyl)silane-titanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)-dimethyl(η^5 -2-methylindenyl)silane-titanium (IV) dimethyl, (t-butylamido)dimethyl(η^5 -2-methyl-indenyl)silane-titanium (IV) dibenzyl, (t-butylamido)-dimethoxy(η^5 -2-methylindenyl)silane-titanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)-dimethoxy(η^5 -2-methylindenyl)silane-titanium (II) 1,3-pentadiene, (t-
30 butylamido)dimethoxy(η^5 -2-methylindenyl)silane-titanium (II) 2,4-hexadiene, (t-

butylamido)dimethoxy(η^5 -2-methylindenyl)-silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)dimethoxy(η^5 -2-methylindenyl)-silanetitanium (IV) dimethyl, (t-butylamido)-dimethoxy(η^5 -2-methylindenyl)silanetitanium (IV) dibenzyl, (t-butylamido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butyl-amido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)-diisopropoxy(η^5 -2-methylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)diisopropoxy(η^5 -2-methylindenyl)-silanetitanium (IV) dimethyl, (t-butylamido)diisopropoxy(η^5 -2-methylindenyl)-silanetitanium (IV) dibenzyl, (t-butylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)-ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (IV) dimethyl, (t-butylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (IV) dibenzyl, (t-butylamido)dimethyl(η^5 -2-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethyl(η^5 -2-ethylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)dimethyl(η^5 -2-ethylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)dimethyl(η^5 -2-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)dimethyl(η^5 -2-ethylindenyl)silanetitanium (IV) dimethyl, (t-butylamido)dimethoxy(η^5 -2-ethylindenyl)silanetitanium (IV) dibenzyl, (t-butylamido)dimethoxy(η^5 -2-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethoxy(η^5 -2-ethylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)dimethoxy(η^5 -2-ethylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)dimethoxy(η^5 -2-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)dimethoxy(η^5 -2-ethylindenyl)silanetitanium (IV) dimethyl, (t-butylamido)dimethoxy(η^5 -2-ethylindenyl)silanetitanium (IV) dibenzyl, (t-butylamido)-diisopropoxy(η^5 -2-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)-diisopropoxy(η^5 -2-ethylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)diisopropoxy(η^5 -2-ethylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butyl-amido)diisopropoxy(η^5 -2-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butyl-amido)diisopropoxy(η^5 -2-ethylindenyl)silanetitanium (IV) dimethyl, (t-butylamido)diisopropoxy(η^5 -2-ethylindenyl)silanetitanium (IV) dibenzyl, (t-butylamido)ethoxymethyl(η^5 -2-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)ethoxymethyl(η^5 -2-ethylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)ethoxymethyl(η^5 -2-ethylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)-ethoxymethyl(η^5 -2-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)-ethoxymethyl(η^5 -2-ethylindenyl)silanetitanium (IV) dimethyl, (t-butylamido)ethoxymethyl(η^5 -2-

- ethylindenyl)silanetitanium (IV) dibenzyl, (t-butylamido)dimethyl(η^5 -2-methyl-s-indacen-1-yl)-
 silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethyl(η^5 -2-methyl-s-indacen-1-
 yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)dimethyl(η^5 -2-methyl-s-indacen-1-yl)-silane-
 titanium (II) 2,4-hexadiene, (t-butylamido)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silane-titanium (III) 2-
 5 (N,N-dimethylamino)benzyl, (t-butylamido)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (IV)
 dimethyl, (t-butylamido)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (t-butyl-
 amido)dimethoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butyl-
 amido)dimethoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)-
 dimethoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)dimethoxy(η^5 -
 10 2-methyl-s-indacen-1-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)dimethoxy-
 (η^5 -2-methyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, (t-butylamido)dimethoxy(η^5 -2-methyl-s-
 indacen-1-yl)silanetitanium (IV) dibenzyl, (t-butylamido)diisopropoxy(η^5 -2-methyl-s-indacen-1-yl)-
 silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)diisopropoxy(η^5 -2-methyl-s-indacen-1-
 yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)diisopropoxy(η^5 -2-methyl-s-indacen-1-yl)silane-
 15 titanium (II) 2,4-hexadiene, (t-butylamido)diisopropoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium
 (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)diisopropoxy(η^5 -2-methyl-s-indacen-1-yl)silane-
 titanium (IV) dimethyl, (t-butylamido)diisopropoxy(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (IV)
 dibenzyl, (t-butyl-amido)ethoxymethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-
 1,3-butadiene, (t-butylamido)ethoxymethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 1,3-
 20 pentadiene, (t-butyl-amido)ethoxymethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 2,4-
 hexadiene, (t-butylamido)-ethoxymethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (III) 2-(N,N-
 dimethylamino)benzyl, (t-butyl-amido)ethoxymethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (IV)
 dimethyl, (t-butylamido)ethoxy-methyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl,
 (t-butylamido)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-
 25 butylamido)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)-
 dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)-dimethyl(η^5 -2-
 ethyl-s-indacen-1-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butyl-amido)dimethyl(η^5 -2-
 ethyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, (t-butylamido)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)-
 silanetitanium (IV) dibenzyl, (t-butyl-amido)dimethoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II)
 30 1,4-diphenyl-1,3-butadiene, (t-butyl-amido)dimethoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II)
 1,3-pentadiene, (t-butylamido)-dimethoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II) 2,4-
 hexadiene, (t-butylamido)dimethoxy(η^5 -2-ethyl-s-indacen-1-yl)silane-titanium (III) 2-(N,N-dimethyl-
 amino)benzyl, (t-butylamido)dimethoxy(η^5 -2-ethyl-s-indacen-1-yl)-silanetitanium (IV) dimethyl, (t-
 butylamido)dimethoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (t-butylamido)-

- diisopropoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)-
 diisopropoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)-
 diisopropoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)diisopropoxy-
 (η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (III) 2-(N,N-dimethylamino)-benzyl, (t-butylamido)-
 5 diisopropoxy(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, (t-butyl-amido)diisopropoxy(η^5 -
 2-ethyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (t-butylamido)ethoxy-methyl(η^5 -2-ethyl-s-
 indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)ethoxy-methyl(η^5 -2-ethyl-s-
 indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)ethoxymethyl(η^5 -2-ethyl-s-indacen-1-
 yl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)ethoxymethyl(η^5 -2-ethyl-s-indacen-1-yl)silane-
 10 titanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)ethoxymethyl(η^5 -2-ethyl-s-indacen-1-
 yl)silanetitanium (IV) dimethyl, (t-butylamido)ethoxymethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium
 (IV) dibenzyl, (dimethylamine)dimethyl(η^5 -2-methylindenyl)silanetitanium (III) dimethyl,
 (dimethylamine)-dimethyl(η^5 -2-methylindenyl)silanetitanium (III) dibenzyl, (diisopropylamine)-
 dimethyl(η^5 -2-methylindenyl)silanetitanium (III) dimethyl, (diisopropylamine)dimethyl(η^5 -2-
 15 methylindenyl)-silanetitanium (III) dibenzyl, (di-n-butylamine)dimethyl(η^5 -2-methylindenyl)silane-
 titanium (III) dimethyl, (di-n-butylamine)dimethyl(η^5 -2-methylindenyl)silanetitanium (III) dibenzyl, (di-
 iso-butylamine)dimethyl(η^5 -2-methylindenyl)silanetitanium (III) dimethyl, (di-iso-butylamine)dimethyl-
 (η^5 -2-methylindenyl)silanetitanium (III) dibenzyl, (dimethylamine)dimethyl(η^5 -2-methyl-s-indacen-1-
 yl)silanetitanium (III) dimethyl, (dimethylamine)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium
 20 (III) dibenzyl, (diisopropylamine)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silane-titanium (III) dimethyl,
 (diisopropylamine)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (III) dibenzyl, (di-n-butyl-
 amine)dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (III) dimethyl, (di-n-butylamine)-
 dimethyl(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (III) dibenzyl, (di-isobutyl-amine)dimethyl(η^5 -2-
 methyl-s-indacen-1-yl)silanetitanium (III) dimethyl, (di-isobutylamine)-dimethyl(η^5 -2-methyl-s-
 25 indacen-1-yl)silane-titanium (III) dibenzyl, (dimethylamine)dimethyl(η^5 -2-ethylindenyl)silanetitanium
 (III) dimethyl, (dimethylamine)dimethyl(η^5 -2-ethylindenyl)silane-titanium (III) dibenzyl, (diisopropyl-
 amine)dimethyl(η^5 -2-ethylindenyl)silanetitanium (III) dimethyl, (diisopropylamine)dimethyl(η^5 -2-
 ethylindenyl)silane-titanium (III) dibenzyl, (di-n-butylamine)-dimethyl(η^5 -2-ethylindenyl)silanetitanium
 (III) dimethyl, (di-n-butylamine)dimethyl(η^5 -2-ethyl-indenyl)silanetitanium (III) dibenzyl, (di-isobutyl-
 30 amine)dimethyl(η^5 -2-ethylindenyl)silanetitanium (III) dimethyl, (di-iso-butylamine)dimethyl(η^5 -2-
 ethylindenyl)silanetitanium (III) dibenzyl, (dimethylamine)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silane-
 titanium (III) dimethyl, (dimethylamine)-dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (III)
 dibenzyl, (diisopropylamine)-dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (III) dimethyl,
 (diisopropylamine)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (III) dibenzyl, (di-n-butylamine)-

dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (III) dimethyl, (di-n-butylamine)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (III) dibenzyl, (di-iso-butylamine)dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (III) dimethyl, (di-iso-butylamine)-dimethyl(η^5 -2-ethyl-s-indacen-1-yl)silanetitanium (III) dibenzyl, or group B that includes (t-butyl-amido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II)

5 1,4-diphenyl-1,3-butadiene, (t-butyl-amido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butyl-amido)dimethyl(η^5 -2,3-dimethyl-indenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butyl-amido)dimethyl(η^5 -2,3-dimethyl-indenyl)silanetitanium (IV) dimethyl, (t-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dibenzyl, (t-butylamido)dimethoxy(η^5 -2,3-dimethylindenyl)-

10 silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)-dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)-dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dimethyl, (t-butylamido)-dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dibenzyl, (t-butylamido)-

15 diisopropoxy(η^5 -2,3-dimethylindenyl)-silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)-diisopropoxy-(η^5 -2,3-dimethylindenyl)-silanetitanium (II) 1,3-pentadiene, (t-butylamido)-diisopropoxy(η^5 -2,3-dimethylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)diisopropoxy-(η^5 -2,3-dimethyl-indenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dimethyl, (t-butylamido)diisopropoxy(η^5 -2,3-

20 dimethylindenyl)-silanetitanium (IV) dibenzyl, (t-butyl-amido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butyl-amido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silane-titanium (II) 1,3-pentadiene, (t-butylamido)-ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)ethoxy-methyl(η^5 -2,3-dimethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)-ethoxymethyl(η^5 -2,3-

25 dimethylindenyl)silanetitanium (IV) dimethyl, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dibenzyl, (t-butylamido)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (II) 2,4-hexadiene, (t-butylamido)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) 2-(N,N-

30 dimethylamino)benzyl, (t-butylamido)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, (t-butylamido)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (t-butylamido)dimethoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)dimethoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (II) 2,4-

- hexadiene, (t-butylamido)dimethoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)dimethoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, (t-butylamido)dimethoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (t-butylamido)diisopropoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)diisopropoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)diisopropoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)diisopropoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)diisopropoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, (t-butylamido)diisopropoxy(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, (t-butylamido)ethoxymethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (dimethylamine)dimethyl(η^5 -2,3-dimethyl-indenyl)silanetitanium (III) dimethyl, (dimethylamine)-dimethyl(η^5 -2,3-dimethylindenyl)silane-titanium (III) dibenzyl, (diisopropylamine)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (III) dimethyl, (diisopropylamine)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (III) dibenzyl, (di-n-butylamine)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (III) dimethyl, (di-n-butylamine)-dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (III) dibenzyl, (di-isobutylamine)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (III) dimethyl, (di-isobutylamine)-dimethyl(η^5 -2,3-dimethylindenyl)-silanetitanium (III) dibenzyl, (dimethylamine)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (III) dimethyl, (dimethylamine)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) dibenzyl, (diisopropylamine)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) dimethyl, (diisopropylamine)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silane-titanium (III) dibenzyl, (di-n-butylamine)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) dimethyl, (di-n-butylamine)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) dibenzyl, (di-isobutylamine)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) dimethyl, (di-isobutylamine)dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (III) dibenzyl, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV)

- dibenzyl, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silane-titanium (II) 1,3-pentadiene, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)-dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butyl-
- 5 amido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl, (t-butylamido)-dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethyl-
- 10 indenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)-silanetitanium (IV) dibenzyl, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silane-
- 15 titanium (II) 1,3-pentadiene, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
- (t-butylamido)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-
- 20 butadiene, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, (t-butylamido)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (t-
- 25 butylamido)dimethoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (II) 1,3-pentadiene, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (II) 2,4-hexadiene, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium
- (IV) dimethyl, (t-butylamido)dimethoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (IV)
- 30 dibenzyl, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-
- titanium (II) 1,3-pentadiene, (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)-silanetitanium (II) 2,4-hexadiene (t-butylamido)diisopropoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)-silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)-diisopropoxy(η^5 -2-methyl-3-ethyl-s-

indacen-1-yl)silanetitanium (IV) dimethyl, (t-butylamido)-diisopropoxy(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (t-butylamido)-ethoxymethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (II) 1,3-pentadiene, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (IV) dimethyl, (t-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (IV) dibenzyl, (dimethylamine)dimethyl(η^5 -2-methyl-3-ethyl-indenyl)silane-titanium (III) dimethyl, (dimethylamine)dimethyl(η^5 -2-methyl-3-ethylindenyl)silane-titanium (III) dibenzyl, (diisopropylamine)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) dimethyl, (diisopropylamine)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) dibenzyl, (di-n-butyl-amine)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) dimethyl, (di-n-butylamine)-dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) dibenzyl, (di-iso-butylamine)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) dimethyl, (di-iso-butylamine)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) dibenzyl, (dimethylamine)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (III) dimethyl, (dimethylamine)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silane-titanium (III) dibenzyl, (diisopropylamine)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (III) dimethyl, (diisopropylamine)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (III) dimethyl, (di-n-butylamine)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (III) dimethyl, (di-n-butylamine)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (III) dibenzyl, (di-iso-butylamine)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (III) dimethyl, (di-iso-butylamine)dimethyl(η^5 -2-methyl-3-ethyl-s-indacen-1-yl)silanetitanium (III) dibenzyl.

7. The process of Claim 5, wherein the catalyst is a Group A catalyst selected from (t-butyl-amido)-dimethyl(η^5 -2-methyl-s-indacen-1-yl)silane-titanium (IV) dimethyl, (t-butylamido)-dimethyl-(η^5 -2-methyl-s-indacen-1-yl)silane-titanium (II) 1,3-pentadiene and (t-butylamido)dimethyl-(η^5 -2-methyl-s-indacen-1-yl)silanetitanium (II) 2,4-hexadiene or a Group B catalyst selected from (t-butylamido)-dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene and (t-butyl-amido)-dimethyl(η^5 -2,3-dimethyl-s-indacen-1-yl)silanetitanium (IV) dimethyl.

8. The process of any of Claims 5-7, wherein activating cocatalyst is selected from:
30 trispentafluorophenyl borane, cocatalysts represented by the formula $L^*-H)_d^+ (A)^{d-}$

wherein:

L^* is a neutral Lewis base;

(L*-H)+ is a Brönsted acid; and A^{d+} either (a) is a noncoordinating, compatible anion having a charge of d-, with d being an integer from 1 to 3, or (b) corresponds to the formula: [M'Q₄]⁻;

wherein:

M' is boron or aluminum in the +3 formal oxidation state; and

5 Q is, independently for each occurrence, selected from hydride, dialkylamido, halide, hydrocarbyl, hydrocarbyloxy, halosubstituted-hydrocarbyl, halosubstituted hydrocarbyloxy, and halo- substituted silylhydrocarbyl radicals (including perhalogenated hydrocarbyl- perhalogenated hydrocarbyloxy- and perhalogenated silylhydrocarbyl radicals), said Q having up to 20 carbons with the proviso that in not more than one occurrence is Q a halide;

10 cocatalysts represented by the formula (L*-H)⁺(BQ₄)⁻

wherein

L* is a neutral Lewis base;

B is boron in a formal oxidation state of 3; and

15 Q is a hydrocarbyl-, hydrocarbyloxy-, fluorinated hydrocarbyl-, fluorinated hydrocarbyloxy-, or fluorinated silylhydrocarbyl- group of up to 20 nonhydrogen atoms, with the proviso that in not more than one occasion is Q hydrocarbyl; or

a cocatalyst that is a salt of a carbenium ion and a noncoordinating, compatible anion represented by the formula ©⁺ (BQ₄)⁻

wherein:

20 ©⁺ is a C₁₋₂₀ carbenium ion; and

Q is a hydrocarbyl-, hydrocarbyloxy-, fluorinated hydrocarbyl-, fluorinated hydrocarbyloxy-, or fluorinated silylhydrocarbyl- group of up to 20 nonhydrogen atoms, with the proviso that in not more than one occasion is Q hydrocarbyl.

9. The process of Claim 8, wherein polymerization occurs in the presence of a
25 scavenging compound, the scavenging compound being selected from an aluminoxane and a Group 13 hydrocarbylamide compound according to the formula R¹₂Me(NR²₂), wherein R1 and R2 are independently in each occurrence a C₁₋₃₀ hydrocarbyl, and Me is a Group 13 Metal.

10. The process of claim 9, wherein the scavenging compound is
(bistrimethylsilylamido)diisobutylaluminum

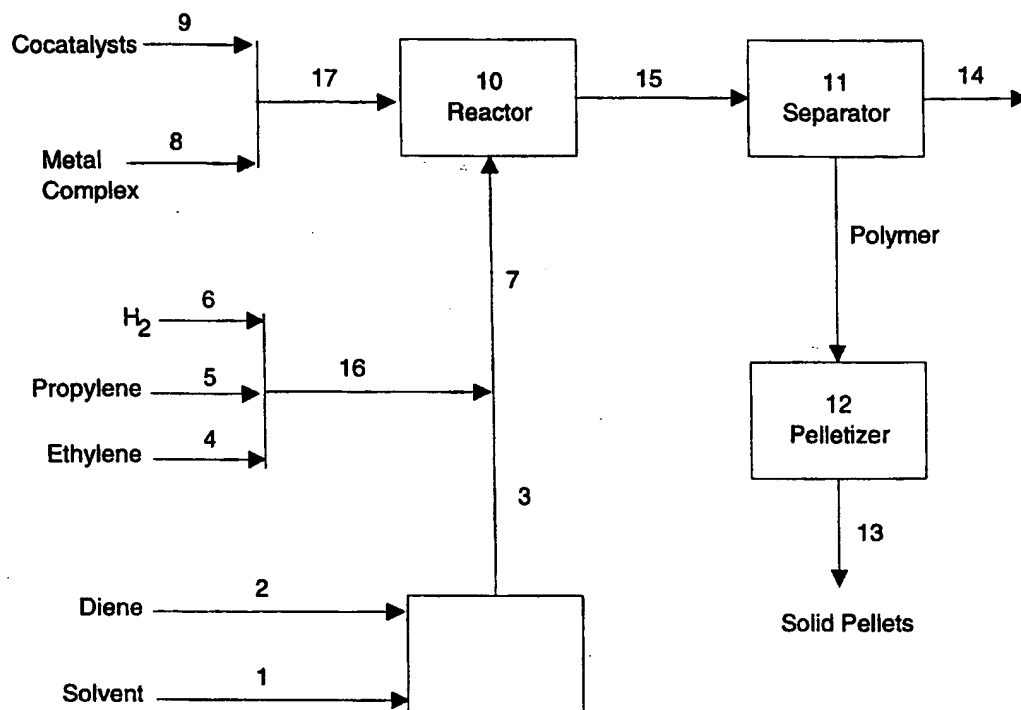
11. The process of Claim 5, wherein the diene is selected from the group consisting of 5-ethylidene-2-norbornene, 5-vinylidene-2-norbornene, 5-methylene-2-norbornene, 1,4-hexadiene, 1,3-pentadiene, dicyclopentadiene, 7-methyl-1,6-octadiene, 1,3-butadiene, 4-methyl-1,3-pentadiene, 5-methyl-1,4-hexadiene, 6-methyl-1,5-heptadiene, norbornadiene, 1,5-octadiene, and
5 1,9-decadiene and contact occurs at a temperature of from about 40°C to about 185 °C.

12. The process of Claim 12, wherein wherein the activating cocatalyst is selected from tris(pentafluorophenyl) borane, di(hydrogenated-tallowalkyl)methylammonium tetrakis-(pentafluorophenyl)borate, tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate, and N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate.

10

Figure 1

Figure 1
Continuous Polymerization Process



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/07252

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F210/18 C08F4/645

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-------------|---|--------------------------------------|
| X A X | US 5 624 878 A (DEVORE DAVID D ET AL) 29 April 1997 see the whole document & WO 95 00526 A cited in the application --- | 5-9, 11, 12 1-4, 10 5-9, 11 |
| X A | US 5 625 016 A (SCHIFFINO RINALDO S ET AL) 29 April 1997 see the whole document --- | 5-9, 11, 12 1-4, 10 |
| A | EP 0 708 117 A (SUMITOMO CHEMICAL CO) 24 April 1996 see page 5, line 34 - page 7, line 18; claims; examples --- | 5-12 |
| A | EP 0 552 946 A (MITSUI PETROCHEMICAL IND) 28 July 1993 see claims; examples --- | 1-4, 11 |
| -/- | | |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

12 December 1997

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21/01/1998

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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